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The Ultraviolet Absorption Spectra of Simple Hydrocarbons

I. *n*-Heptene-3 and Tetramethylethylene

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The ultraviolet absorption spectra of *n*-heptene-3 and tetramethylethylene were measured in liquid and hexane solution phase, between 4000A and 2100A and in vapor phase between 2300A and 1500A. Curves showing the logarithm of the molecular extinction coefficient as a function of the wave number are given for the measurements in the quartz region and tables giving the regions of absorption together with the wave-lengths of the centers of bands for the measurements with the fluorite vacuum spectrograph. Comparison with earlier work shows the progressive shift toward the visible of the absorption bands in the Schumann region as the hydrogen atoms of ethylene are replaced by alkyl groups, and the parallelism between the spectra of different hydrocarbons having the same configuration with respect to the double bond.

DETAILED information regarding the spectroscopic characteristics of compounds containing the carbon-carbon double bond is of importance from the standpoint both of chemical reactivity and of theoretical understanding of the electronic configurations which constitute the ethylenic linkage. Of fundamental importance to these problems is the question of how the energy relationships of the ethylenic configuration are affected by replacement of the hydrogen atoms of ethylene by alkyl radicals.[1] Owing to the complexity of the molecules, ultimate analysis of the spectroscopic data obtained for ethylenic derivatives of this type is not yet possible. Nevertheless, much can be learned from a comparative study of the spectral characteristics of an appropriately selected series of such hydrocarbons, which will eventually contribute to a more specific electronic description of the carbon-carbon double bond.

Systematic investigation of the light absorption of olefine hydrocarbons throughout the region $\lambda=4000$A to $\lambda=1500$A has been undertaken in this laboratory. The present paper covers two substances for which data are complete through the entire range, and for which the results are of particular interest in relation to work already published.[1a] Similar study of several other hydrocarbons is well advanced, and an extensive program is planned which includes, in addition to simple olefines, benzene derivatives, diolefines, conjugated double bond systems, and other related groupings.

EXPERIMENTAL

The wave-length range covered by these investigations is such as to require two types of technique. The absorption in the near ultra-

[1] (*a*) Carr and Stücklen, Zeits. f. physik. Chemie **B25**, 57 (1934); (*b*) Snow and Allsopp, Trans. Faraday Soc. **30**, 93 (1934).

violet, between 3300 and 2500A, has on the order of from one-thousandth to one ten-thousandth the intensity of that in the further ultraviolet. Because of this low intensity the pure liquid hydrocarbons and their hexane solutions were employed for this region of the spectrum rather than the materials in the gaseous state. The procedure for making this type of measurement, which has been fully described by one of us,[2] was followed with minor modifications. The iron electrodes were replaced by copper, and a second spark gap was introduced in series with the copper spark to make the discharge more steady. The photographic plates used were Eastman No. 40 and Eastman Ultraviolet Spectroscopic, the latter making it possible to follow the light absorption very satisfactorily to 2100A.

The far ultraviolet absorption was obtained for the substances in the vapor state at pressures of 10 mm or less, through a column 11.5 cm long. The optical system was a Hilger E419 fluorite vacuum spectrograph. Light from a discharge through hydrogen was passed through the cell fitted with fluorite windows and containing the vapor of the compound to be studied, and thence into the spectrograph. The spaces between the ends of the absorption cell and the lamp and the spectrograph were less than 1 mm in width and were filled with nitrogen. Nitrogen was also used to carry the hydrocarbon vapors in continuous flow through the cell and to provide gaseous shields next to the fluorite ends of the absorption chamber to prevent reaction of the hydrocarbon with the white wax which held the windows in place. These experimental arrangements have been discussed in detail in a report on preceding work from this laboratory.[1a]

Data

The quartz ultraviolet absorption of the two substances under consideration, *n*-heptene-3 and tetramethylethylene, is reported in terms of molecular extinction coefficients, the logarithms of which, when plotted against wave numbers, give the well-known type of absorption curve. The curves in each case are based on about sixty experimental points so closely spaced as to constitute an almost continuous line when plotted on the scale of the figures appearing in the text.

Earlier work in this laboratory on the absorption of ethylenic derivatives below 2300A led to the recognition of three distinct divisions of this portion of their spectra, which were designated as regions *A*, *B* and *C*. Since the results reported in this paper admit of similar classification, the limits and characteristics of the different regions are summarized briefly. From 2300A to about 1850A, there is a region of narrow diffuse bands, the number and position of which depend markedly on the particular hydrocarbon concerned; this is referred to as region *C*. Below this is a region which seemed to show only a broad continuous band with a maximum in the region 1750 to 1800A which was designated as region *B*. Because of the breadth of the band it is not possible to determine the position of the maximum with an accuracy greater than ±15A. Region *A* consists of a second broad structureless band whose maximum cannot be determined with our spectrograph but must be below 1530A. This band is found also in the absorption of saturated hydrocarbons and is associated with the saturated carbon-carbon linkage. The breadth of both *A* and *B* varies greatly with pressure, so that they are frequently observed to merge into one another, giving the impression of continuous absorption below 1800A. The narrow bands in region *C* for the two compounds here reported are very shallow, i.e., they are underlaid by continuous absorption and do not exceed it greatly in intensity. This occasions considerable difficulty in obtaining good exposures of the bands and a rather higher uncertainty in their measurement than is the case, for instance, with benzene which has a much more clearly defined spectrum. Two possible sources of this background may be noted, *viz.*, the narrow bands lie sufficiently close together that their margins may overlap; or the long wave-length side of band *B* may extend throughout this entire region at the pressures necessary to bring out the *C* bands. It seems likely that both factors are operating to some extent; the former more particularly at longer wave-lengths of region *C* and the latter in the shorter wave-length portion.

The limits of accuracy of the values for the location of band centers are probably somewhat

[2] Carr, J. Am. Chem. Soc. **51**, 3041 (1929).

better than ± 75 cm^{-1} at 2300A, ± 60 cm^{-1} at 2100A, and ± 50 cm^{-1} at 1850A. It should be noted that this uncertainty is due to the difficulty in determining the exact point which is to be taken as the center of the band. No estimate of band widths are given, since these vary within fairly wide limits with the pressure of the hydrocarbon vapor. All these bands are diffuse, and within the limits of the dispersion (250 cm^{-1} per mm at 2100A and 200 cm^{-1} at 1850A) show no indication of heads or of fine structure. The relative intensities of bands or regions of absorption cannot be determined with precision by the method of measurement which we have used. An approximate estimate can be made, however, by comparison of the exposures taken with different pressures of the hydrocarbon vapors, and such estimates for each compound are given in the form of a curve in Fig. 2.

N-heptene-3

N-heptene-3 employed for this study was prepared in this laboratory under the direction of M. L. Sherrill.[3] Fig. 1 shows the quartz ultraviolet absorption curve for this substance in the pure state and in hexane solution. With lengths of absorbing column (d) which varied from 0.2 to 7.0 cm, the absorption of the pure hydrocarbon could be followed from log $\epsilon = -2.00$ to -0.60. A 0.428 molar solution gave the absorption to log $\epsilon = 0.90$, and the remainder of the curve was obtained from a second dilution to 0.034 molar. Notable features of the absorption curve (Fig. 1) are its long wave-length limit which lies at about 35,200 cm^{-1}, the step-out extending from the beginning of absorption to approximately 39,000 cm^{-1} which indicates the presence of a low intensity band, the second wide step-out between 42,000 and 46,000 cm^{-1}, which is due to another band of much higher intensity, and the final sharp rise in intensity of absorption which continues uninterrupted to 47,200 cm^{-1}. The absorption curve is markedly affected by the presence of so-called peroxide substances which form in most olefinic hydrocarbons. For this

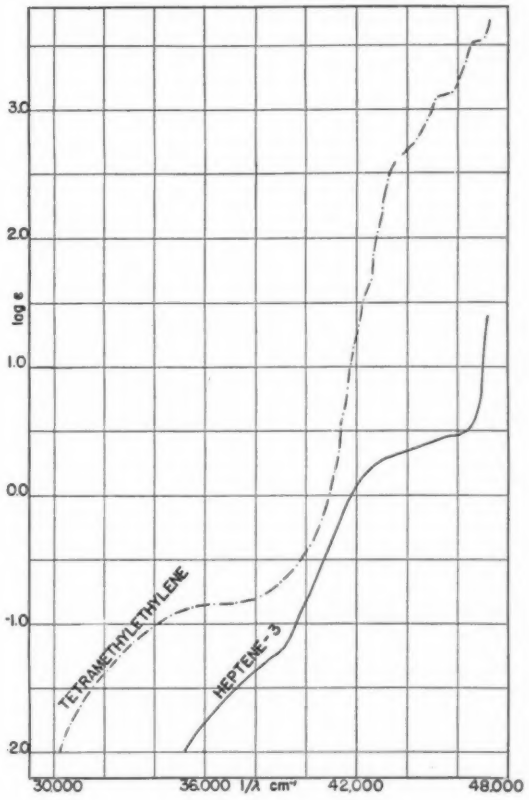

FIG. 1.

reason the absorption was studied immediately after distillation from sodium, and with minimum exposure to air during transfers and dilution. The material used for the absorption study was therefore originally peroxide free, and when tested afterwards for presence of peroxide showed only very slight traces.[4]

Absorption by gaseous *n*-heptene-3 in the far ultraviolet shows in region *C* three discrete bands and a fourth step-out which precedes the last band and indicates the existence of a fourth band. The position of these bands and of the step-out are given in Table I. The qualitative estimate of relative intensity of absorption in the far ultraviolet region is indicated in Fig. 2.

Tetramethylethylene

We are indebted to Professor F. C. Whitmore of Pennsylvania State College for supplying a sample of tetramethylethylene for these spectro-

[3] The synthesis of 4-heptanol and the preparation of the heptene by dehydration of the alcohol with sulphuric acid was carried out by Joyce J. Wadmond. Her data on the physical constants are as follows: b.p. 95.7–95.8° at 760 mm, d^{20}_4 0.7001, n^{20}_D 1.4041.

[4] The ferrous sulphate ammonium thiocyanate test was used for determining the presence of peroxide.

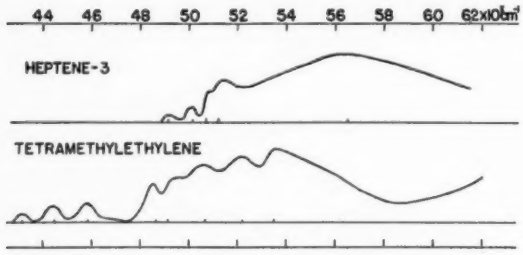

FIG. 2.

graphic investigations.[5] Fig. 1 shows the absorption curve of this substance in the quartz ultraviolet region. The points up to log $\epsilon = -0.4$ were obtained from the pure liquid hydrocarbon; up to log $\epsilon = 1.00$ from a 0.34 molar hexane solution; up to log $\epsilon = 2.00$ from a 0.034 molar solution; to log $\epsilon = 3.00$ from a 0.0034 molar solution, and the remaining points from a 0.0004 molar solution. The beginning of absorption for this substance is at 30,200 cm^{-1} from which point a broad step-out indicating a band of low intensity extends to about 39,000 cm^{-1}. Beyond 40,000 cm^{-1} the intensity of absorption rises sharply to about 43,400 cm^{-1} where lies the first of the narrow bands observed in the vapor spectrum. Three of these bands can be identified between this point and 47,300 cm^{-1}. This compound has the tendency already noted as characteristic of ethylenic hydrocarbons to form peroxides, and was therefore treated with the same precautions as were used for *n*-heptene-3.

In the *C* region, the absorption is characterized by the presence of six narrow diffuse bands together with a sharp step-out indicating another band, the wave-lengths and wave numbers of the centers of the bands are given in Table II. In this compound, region *B* is shifted toward the visible to such an extent that it overlaps the last three or four bands of *C* so that the measurement of these bands is somewhat more uncertain than is the case with the other bands and the determination of the maximum of the broad band *B* is difficult.

TABLE I. *Far ultraviolet absorption of n-heptene-3.*

A		*B*		*C*	
A	cm^{-1}	*A*	cm^{-1}	*A*	cm^{-1}
<1530	>65,400	1750–1720	57,140–58,000	2035 1995 (1972) 1953	49,140 50,120 (50,700) 51,200

[5] Physical constants for the material which we used are the following: b.p. 73.2–73.5° at 760 mm; $n^{20}D$ 1.41198.

A comparison of the positions of the three narrow bands observed in the hexane solutions of tetramethylethylene with those of the corresponding bands in the vapor spectrum is made in Table III. The wave number at which the curve of the hexane solution shows the sharp change in shape at the beginning of a step-out is chosen for comparison with the band centers in the vapor phase. Such a choice is more or less arbitrary but gives a comparable point for the three bands. The values of the extinction coefficient give a dependable basis for comparison of the intensities in the vapor phase measurements.

DISCUSSION OF RESULTS

The types of ethylenic derivatives which have been studied previously in this laboratory together with these two additional compounds are

$$\begin{matrix} & H & H & \\ R- & C & = & C \\ & H & & \end{matrix} \quad (n\text{-pentene-1, } n\text{-heptene-1})$$

$$\begin{matrix} & H & H & \\ R- & C & = & C-R' \end{matrix} \quad (n\text{-pentene-2, } n\text{-heptene-3})$$

$$\begin{matrix} & R & H & \\ R- & C & = & C-R \end{matrix} \quad (\text{trimethylethylene})$$

$$\begin{matrix} & R & R & \\ R- & C & = & C-R \end{matrix} \quad (\text{tetramethylethylene}).$$

The complete ultraviolet absorption of these six compounds can be classified into the three regions previously described together with a fourth region, designated as *D*, which includes the quartz measurements between 3300 and 2100A.

These four regions of absorption can be seen in all the ethylenic hydrocarbons and would indicate the existence of a similarity in their elec-

TABLE II. *Far ultraviolet absorption of tetramethylethylene.*

A		*B*		*C*	
A	cm^{-1}	*A*	cm^{-1}	*A*	cm^{-1}
<1530	>65,400	max. 1870	53,480	2318 2248 2181 2056 (1995) 1973 1916	43,140 44,480 45,850 48,640 (50,110) 50,670 52,200

tronic transitions. Certain conclusions concerning the relationship of the electronic band systems of ethylenic derivatives to those of ethylene are suggested by these results but will be considered in a later paper from this laboratory. The point of special interest in the present study is the number and position of the absorption bands in region *C* and their relation to the structure of the hydrocarbon molecule. In the earlier study of three pentenes and one heptene[1a] two important relationships between molecular configuration and absorption spectra were evident; (1) the spectra of *different* hydrocarbons having the same arrangement of alkyl groups around the double bond are almost identical, (2) the position of the first absorption band in the Schumann region is characteristic of the number of alkyl groups around the double bond and is shifted progressively toward the visible as the number of alkyl groups increase. The study of 3-heptene and tetramethylethylene adds one hydrocarbon of similar structure to those already studied, and one of a type not previously examined. The relationship between the bands in region *C* of the six aliphatic hydrocarbons and benzene are given in Fig. 3.

Comparison of the spectra of the group of olefines having the configuration $C-\overset{H}{C}=\overset{H}{C}-C$ with that of benzene shows a striking similarity in the position of the first band and points to the conclusion that this grouping, which is also common to the benzene molecule, must be an influencing factor in determining the position of the first absorption band of benzene as well as of the aliphatic series.

TABLE III. *Comparison of ultraviolet absorption of tetramethylethylene in the vapor state and in hexane solution.*

Vapor		Solution (0.0004 M)	
A	cm^{-1}	*A*	cm^{-1}
2318	43,140	2304	43,400
2248	44,480	2217	45,100
2181	45,850	2155	46,500

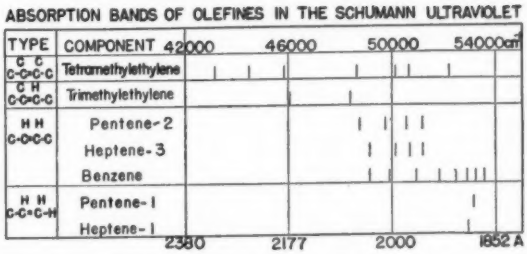

FIG. 3. (The heading of the second column should be "Compound.")

The absorption spectrum of tetramethylethylene is the first hydrocarbon of the type $\overset{C}{C}-C=\overset{C}{C}-C$ whose absorption spectrum has been studied in this region. The pronounced shift to longer wave-lengths of the first band is in agreement with what would be expected from the progressive displacement toward the visible which was previously found for the first absorption band of the pentenes as the hydrogen atoms around the double bond are replaced by alkyl groups.

Certain other characteristics of these vapor spectra will be taken up in a later paper when data from the study of a large number of closely related hydrocarbons are analyzed in detail.

The absorption spectra of the hydrocarbons in liquid and solution as measured with the quartz spectrograph show exactly the same relationship between the different types of groupings as are evident in the Schumann region. The absorption curve for heptene-3 parallels very closely that of pentene-2[6] while the beginning of absorption in the different hydrocarbons as measured by the wave number corresponding to an extinction coefficient, $\log \epsilon = -2.0$ shows a progressive shift toward the longer wave-lengths in going from pentene-1 to tetramethylethylene.

[6] M. L. Sherrill and G. F. Walter, J. Am. Chem. Soc. **58**, 742 (1936).

The Ultraviolet Absorption Spectra of Simple Hydrocarbons

II. In Liquid and Solution Phase

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Molecular extinction coefficients for twelve olefine hydrocarbons have been determined between $\lambda = 3300$A and 2100A and are given in the form of curves showing the logarithm of the extinction coefficient as a function of the wave number. The beginning of absorption, as measured by $\log \epsilon = -2.0$, is quite characteristic of the number of alkyl groups bound to the carbon atoms of the double bond and is only very slightly affected by the nature of the alkyl group.

IN the preparation of highly purified hydrocarbons for absorption spectra measurements in the Schumann region it has been found that the reproducibility of an absorption curve for a given hydrocarbon as measured in liquid phase and hexane solution with a quartz spectrograph, gives an excellent test for the purity of the compound as well as furnishing experimental data of importance in the spectroscopic analysis of these compounds. This paper summarizes the results of such measurements on twelve hydrocarbons, six of which have been reported previously from this laboratory.[1] Nine of the twelve compounds were prepared in this laboratory and the other three, tetramethylethylene and the two diisobutylenes were given us in very pure form by Professor F. C. Whitmore of Pennsylvania State College. Since the fundamental purpose of this investigation is to make a systematic study of the relation between the ultraviolet absorption spectra of an ethylenic hydrocarbon and the position of the double bond in the molecule it is evident that the compounds must be of the highest possible purity. Ultraviolet absorption spectra measurements were made at different stages in the purification of the compounds and purification was continued until the absorption curves after two distillations were identical.

PREPARATION OF COMPOUNDS

The preparation and purification of the hydrocarbons has been carried out by different workers under the general direction of Professor Mary L. Sherrill of this laboratory.[2] Four of the compounds were prepared by dehydration of an alcohol, this method being used in the case of alcohols which are least likely to give a mixture of hydrocarbons on dehydration by sulphuric acid; for example, *n*-pentene-2 from diethyl carbinol, *n*-heptene-3 from dipropyl carbinol, trimethylethylene from tertiary amyl alcohol, methyl diethylethylene from triethyl carbinol. With the exception of tertiary amyl alcohol, where the commercial product was used, the alcohols were prepared in this laboratory by Grignard syntheses. In the case of the other hydrocarbons, the brom-ether synthesis of olefine hydrocarbons, developed by Boord and coworkers,[3] has been found to be most satisfactory. A detailed description of the preparation and purification of 2-methylbutene-1 by this method has already been published.[4] The other hydrocarbons which were synthesized by the Boord method involve fewer reactions for the brom-ether preparation but the method of purification of the hydrocarbon by azeotropic distillation with alcohol through a Crismer column and subsequent fractionations of the hydrocarbon through a Fenske column has been practically the same throughout all the preparations.

In the earlier preparations, the hydrocarbons were refluxed and distilled over sodium during the final purification but the treatment with sodium has been discontinued since the hydrocarbons seemed to form peroxides more readily after distillation from sodium. The effect of

[1] Sherrill and Walter, J. Am. Chem. Soc. **58**, 742 (1936); Carr and Walker (Part I of this series).

[2] Sherrill, Otto and Pickett, J. Am. Chem. Soc. **51**, 3023 (1929); Sherrill, Mayer and Walter, ibid. **56**, 926 (1934); Sherrill and Walter, ibid. **58**, 742 (1936).

[3] Boord and co-workers, J. Am. Chem. Soc. 1930 to date.

[4] Sherrill and Walter, reference 2.

TABLE I.

Compound	b.p. °C, 760 mm	n_D^{20}	d_4^{20}
Pentene-1	30.1 ±0.05	1.3710	0.6410
Pentene-2 (symmetrical methylethylethylene)	36.40±0.05	1.3797	0.6505
2-Methylbutene-1 (unsymmetrical methylethylethylene)	31.05±0.05	1.3777	0.6504
3-Methylbutene-1[1] (isopropylethylene)	20.20±0.03	1.3675 (15°)	0.6323 (15°)
2-Methylbutene-2 (trimethylethylene)	38.42±0.05	1.3878	0.6620
Hexene-3[2a] (symmetrical diethylethylene)	66.70±0.05	1.3947	0.6785
2-3-Dimethylbutene-2 (tetramethylethylene)	73.35±0.10	1.41198	
Heptene-1	93.45±0.05	1.3991	0.6970
Heptene-3 (symmetrical ethylpropylethylene)	95.75±0.05	1.4041	0.7001
3-ethylpentene-2[2b] (methyldiethylethylene)	95.2	1.4140	0.7222
2-4-4-Trimethylpentene-2[3] (diisobutylene II)	105.15±0.05	1.4161	0.7211
2-4-4-Trimethylpentene-1[3] (diisobutylene I)	101.6 ±0.10	1.4083	0.7151

[1] Prepared by the reduction of 1-bromo-2-ethoxy-3-methylbutane with zinc. In the course of hydrogenation experiments on our hydrocarbon by Kistiakowsky and co-workers in the Harvard laboratory, freezing point measurements were attempted but the freezing point is evidently below the temperature of liquid air. Freezing point determinations of the hydrogenation product, however, gave a very sharp freezing point indicating that the isopropylethylene was a very pure product. (Private communication.)

[2] Prepared, and physical constants, including absorption spectra, determined by (a) K. B. Nisbet, (b) C. Monod, in partial fulfillment of the requirements for the M.A. degree.

[3] Prepared by Whitmore and co-workers by dehydration of tertiary butyl alcohol. See J. Am. Chem. Soc. **54**, 3706 (1933).

treatment with sodium is still under investigation in this laboratory. The satisfactory agreement in the physical constants of our preparations with those reported by Kistiakowsky and co-workers,[5] for which detailed descriptions of their methods are given, shows the high degree of purity obtained. Table I gives the physical constants for all the compounds whose absorption spectra are reported in this paper.

ABSORPTION SPECTRA MEASUREMENTS

The extinction coefficients were measured in the region 3500 to 2100A by the photographic comparison method developed by Henri.[6] The spectrograph is a Hilger quartz instrument (E–2) and the light source a condensed spark between copper electrodes. For the short ultraviolet region a condensed spark between a copper and silver electrode has been used recently. Uniform time of 10 seconds for the exposure through the standard, i.e., 1–2 mm thickness of spectrographic hexane in the case of the pure liquid hydrocarbons, or with the hexane solutions, the same thickness of hexane as for the solution with which it is compared, and an exposure of 40 sec. and 60 sec. through each thickness of the hydrocarbon were used throughout. In some cases these times were lengthened for the short ultraviolet region but the same ratio was retained. Baly tubes of fused quartz were used for all the measurements, the length of the absorbing column being varied from 7 to 0.2 cm. The extinction coefficients from $\log \epsilon = -2.0$ to about -0.5 were determined with the pure liquid hydrocarbon, while hexane solutions varying in concentration from 0.8 molar to 0.0003 molar were used for the higher values of $\log \epsilon$. The photographic plates were Eastman No. 40 and Ultraviolet Spectroscopic. Each curve is based on from fifty to seventy experimental points but they are not shown on the curves since they are so closely spaced as to give almost a continuous line. The curves are plotted in the usual way with the logarithm of the molecular extinction coefficient on the ordinate and wave number on the abscissa. The absorption curves for the five pentenes are given in Fig. 1. Pentene-2 represents an equilibrium mixture of the *cis* and *trans* forms since our distilling column was not efficient enough to separate these isomers.[7] This is no doubt true of the two other hydrocarbons which can exist as geometrical isomers, *n*-heptene-3 and *n*-hexene-3.

DISCUSSION

It will be noted that all of the pentenes (Fig. 1) show somewhat similar absorption curves although there are certain characteristics which differentiate the five isomers. The existence of two step-outs, which result from the overlapping of an absorption band of lower intensity with a more intense one, is evident in each of the curves.

Whether the higher intensity step-out which comes at shorter wave-lengths is characteristic of the olefine hydrocarbons or whether it is due to a trace of an impurity, not detected by other methods, is still under investigation in this laboratory. Long refluxing over sodium, or repeated distillations from sodium, especially if the hydrocarbon has stood some weeks or months after

[5] Kistiakowsky, Ruhoff, Smith and Vaughan, J. Am. Chem. Soc. **58**, 137 (1936).

[6] V. Henri, *Études de Photochimie* (Gauthier, Villars et Cie., Paris, 1919). Cf. E. P. Carr, J. Am. Chem. Soc. **51**, 3041 (1929).

[7] Results of hydrogenation experiments carried out on this product by Kistiakowsky and co-workers in the Harvard Laboratory indicate it to be a mixture of the two isomers. J. Am. Chem. Soc. **58**, 137 (1936).

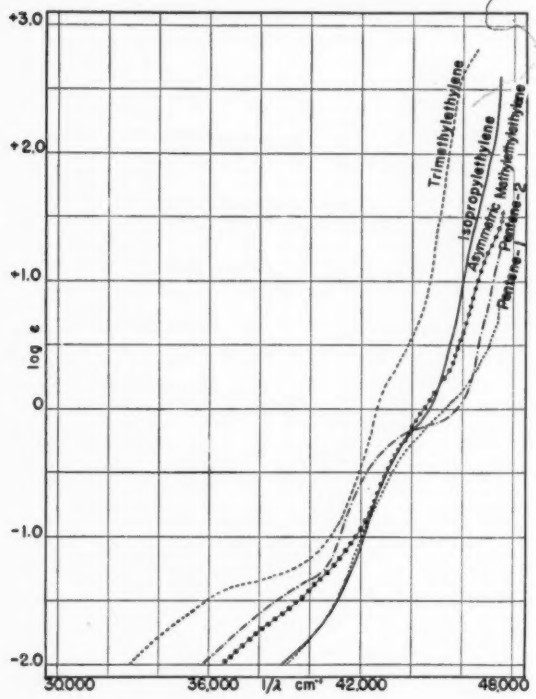

FIG. 1.

preparation, gradually lowers the extinction coefficient at which this step-out appears although the rest of the curve shows no appreciable change in the absence of peroxides. Where peroxides are present the beginning of absorption is shifted markedly toward the visible and the intensity of the first step-out is increased. The change in intensity of the second step-out has been studied particularly with trimethylethylene; by repeated treatment with sodium curves have been obtained which show only a single broad step-out and are in excellent agreement with those obtained by other investigators,[8] but a freshly prepared sample, not subjected to long treatment with sodium always shows a step-out of somewhat higher intensity between 42,000 and 45,000 cm^{-1}. In all of the hydrocarbons this is the region of the spectra where the exact reproducibility of the curves for different samples of the same hydrocarbon is most difficult. Because of the possibility of molecular rearrangement due to prolonged heating with sodium this treatment has been avoided and either azeotropic fractionations with alcohol or repeated fractionations of the hydrocarbon alone have been carried out until absorption curves showed no change on distillation. The reproducibility of the absorption curve is a much more delicate test for the purity of an olefine hydrocarbon than any of the other physical constants. The possibility of the presence of minute quantities of a diene has been considered and is under investigation. Because of the very great intensity of the diene band in the region 42,000–45,000 cm^{-1} [9] as little as 1 part in 10,000 would be amply sufficient to account for the increased absorption in this region and yet give no evidence in any of the other physical constants. Whether or not this step-out is characteristic of a hydrocarbon containing one C=C linkage, or is because of minute traces of a very absorptive impurity, the position of the band does not change with the different isomers as is true with the band of low intensity which gives the step-out at longer wave-lengths.

The position of the low intensity band is the most significant result of the absorption spectra studies in this region. Consideration of the curves for the pentenes shows that the position of this band is characteristic of the number and to a less extent the arrangement of the alkyl groups around the double bond. There is a progressive shift toward the visible as the number of hydrogen atoms bound to the carbon atoms of the double bond is decreased. Since in the case of a step-out there is no definite point for comparison as is true with the maximum of an absorption band, the beginning of absorption as measured at $\log \epsilon = -2.00$ on our curves has been arbitrarily chosen for comparison between the different hydrocarbons. Pentene-1 and isopropylethylene with the same arrangement of hydrogen and alkyl groups around the double bond begin at exactly the same place, 39,000 cm^{-1}, but differ in the short wave region. The effect of two alkyl groups on different carbon atoms, as compared with the two groups on the same carbon atom is shown by the curves for pentene-2 and 2-methylbutene-1 where the two curves are quite similar but that for the latter beginning slightly to the ultraviolet, 35,400 cm^{-1}, as compared with

[8] Luthy, Zeits. f. physik. Chemie **107**, 285 (1923); Allsopp and Snow, Trans. Faraday Soc. **30**, Part **1**, 93 (1934).

[9] Int. Crit. Tab. **5**, 364.

pentene-2 at 35,800 cm^{-1}. Finally when there are three alkyl groups as in trimethylethylene the absorption at log $\epsilon = -2.00$ is at 32,800 cm^{-1}.

This same relationship between the position of the low intensity absorption band and the number of alkyl groups around the double bond is shown in the absorption curves for the three hexenes and three heptenes given in Fig. 2.[10]

It is of interest to note the comparatively slight influence on the absorption curve of a change in alkyl groups which is shown by the close similarity of analogous molecular configurations; for example, pentene-1 and heptene-1, pentene-2, hexene-3, and heptene-3 and trimethylethylene and methyl-diethylethylene. The intensities at which the step-outs occur differ but the position of the low intensity band as measured by log $\epsilon = -2.00$ parallels very closely those of the corresponding pentenes, while that of tetramethylethylene is shifted toward the visible as would be

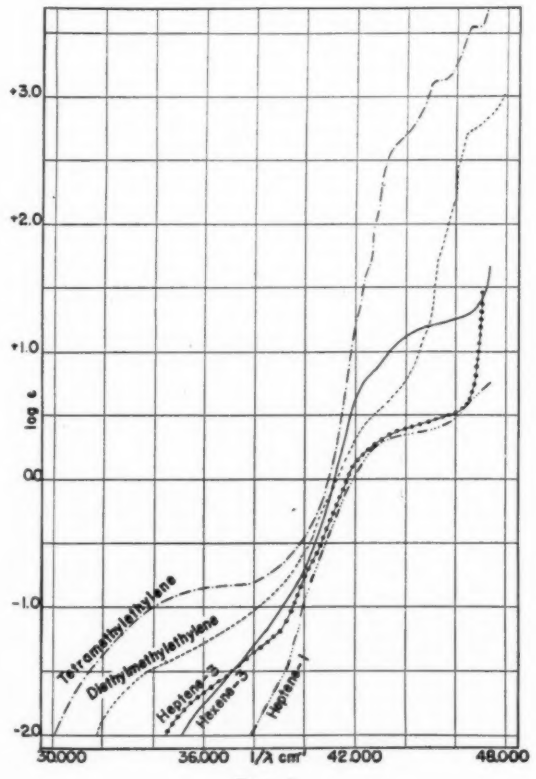

FIG. 2.

[10] Curves for tetramethylethylene and heptene-3 are reproduced from the earlier paper in this series. See Carr and Walker, J. Chem. Phys. this issue.

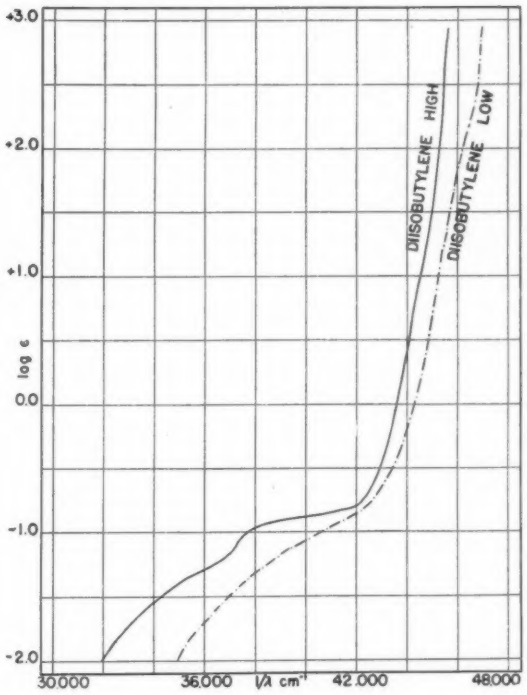

FIG. 3.

expected. In Fig. 3 are given the curves for the two diisobutylenes supplied for this investigation by Whitmore and co-workers. Had the constitutional formulas not been known from chemical methods it is evident from the analogy to the curves of the other hydrocarbons, that the number of alkyl groups around the double bond could be predicted. The nature of the alkyl substituents has practically no influence in determining the position of the absorption band since the curves of diisobutylene high, with the tertiary butyl group, and diisobutylene low, with the highly branched neopentyl group, show the beginning of absorption at the same position as compounds of similar configuration having the methyl or ethyl group in the corresponding position. The difference between symmetrical and unsymmetrical substitution by two alkyl groups cannot be distinguished unless both compounds are known in which case the absorption of the unsymmetrically substituted hydrocarbon is shifted slightly to the ultraviolet in relation to the other. On the basis of these absorption curves the relation between molecular configuration and the beginning of the

weak absorption band in the quartz region may be summarized as follows:

Configuration	$\log \epsilon = -2.00$
H H R−C=C−H	38,000–39,000 cm^{-1}
H H R−C=C−R	34,500–35,800 cm^{-1}
R H R−C=C−H	35,000–36,400 cm^{-1}
R R R−C=C−H	32,000–32,800 cm^{-1}
R R R−C=C−R	30,000 cm^{-1}

The possible theoretical significance of these results will be discussed in the following paper in connection with the study of the absorption spectra of these same compounds in the Schumann region.

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The Ultraviolet Absorption Spectra of Simple Hydrocarbons

III. In Vapor Phase in the Schumann Region

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Absorption spectra measurements between $\lambda = 2300$A and 1500A were made for fourteen ethylenic hydrocarbons, which included four butenes, five pentenes, one hexene, two heptenes and two octenes. A comparative study of these results together with those from the earlier papers in the series has shown the existence of certain general relationships between the absorption spectra of all ethylenic derivatives. The number of alkyl groups bound to the carbon atoms of the C=C bond determines the wave number of the first absorption band; there is a progressive shift toward the visible with increasing number of alkyl groups but the nature of the alkyl group has almost no influence on the position of the first band; where two alkyl groups are bound to the same carbon atom (unsymmetrical substitution) or to different carbon atoms (symmetrical substitution), the wave number of the first band is very slightly different. The first band of these derivatives is tentatively assigned to an electronic excitation corresponding to the transition $^1A_1 \rightarrow {}^1B_1$, predicted for the ethylene molecule. Usually one, but never more than three bands of this system could be seen because of overlapping with another group of bands of higher intensity. All of the sixteen olefines have this same intensity change, showing the existence of another electronic excitation. A third group of bands corresponding to a third electronic excitation can be seen clearly in the spectra of four hydrocarbons and may possibly be present but overlapping the lower frequency group in the other compounds. The bands are too broad and diffuse to admit of analysis of vibrational structure but certain recurring separations, which are probably related to the 1350 cm^{-1} vibrational frequency of ethylene, are evident. In the molecules of higher symmetry, where fewer transitions are permitted by the selection rules, there is less overlapping and therefore more discrete bands can be seen.

INTRODUCTION

IN the description of the electronic structure of polyatomic molecules in their normal and excited states, the principle of molecular orbitals as derived from the linear combination of atomic orbitals has been applied, particularly by Mulliken, to the interpretation of the carbon-carbon double bond of organic chemistry and a detailed theoretical analysis of the orbital structure of the C=C double bond in ethylene has been worked out.[1] Since the method depends primarily on the symmetry conditions of the nuclear frame work of the molecule, a spectroscopic study of a number of closely related ethylenic derivatives should give the experimental data which are necessary to test the theoretical deductions both for ethylene and its derivatives.[2] For some years an extensive study of ethylene hydrocarbons has been in progress in this laboratory and this paper correlates the results of earlier measurements of six ethylenic derivatives in the Schumann region and reports the results for ten additional olefine

[1] Mulliken, Phys. Rev. **41**, 49, 741 (1932); ibid. **43**, 279 (1933); J. Chem. Phys. **3**, 517 (1933).

[2] Snow and Allsopp, Trans. Faraday Soc. **30**, Part 1, 93 (1934).

hydrocarbons. The absorption spectra of four butenes,[3] five pentenes, two hexenes, three heptenes and two octenes have been measured.

The experimental set-up for these determinations was substantially the same as that described previously.[4] The essential features of the apparatus are shown by diagram on Fig. 1. In the present study a longer absorption tube (60 cm) was substituted for those used in the earlier work in order that the partial pressure of the hydrocarbon vapor under examination might be sufficiently low to bring out more bands than were evident at higher pressures. All of the hydrocarbons which had previously been studied were reexamined and in some cases additional bands were noted. The partial pressure of the hydrocarbon in the absorption tube cannot be measured exactly but it can be estimated and pressure changes regulated by careful control of the temperature of the bath (from $-78°C$ to room temperature) in which the bulb containing the liquid hydrocarbon was immersed, by changing the length and width of the capillary through which the stream of nitrogen saturated with gaseous hydrocarbon flowed into the absorption tube and also by control of the difference in pressure between the absorption tube and the bulb containing the liquid hydrocarbon. The partial pressure of the absorbing vapor varied from 50 mm to less than 0.1 mm. All the bands that are given in the following tables were photographed while the vapor was kept flowing through the absorption cell. This was an essential precaution since when the vapor is stationary or flowing very slowly there is considerable photochemical decomposition of the hydrocarbon which is readily evidenced by the appearance of new bands in the spectrum. In some cases these disintegration products could be identified spectroscopically (C_2H_4, C_2H_2), but these bands were easily differentiated from those of the pure hydrocarbon under investigation. A later paper will deal with a spectroscopic study of the disintegration products of the olefines; the investigation of each hydrocarbon was made under conditions which gave photochemical decomposition as well as with flowing vapor where no disintegration took place.

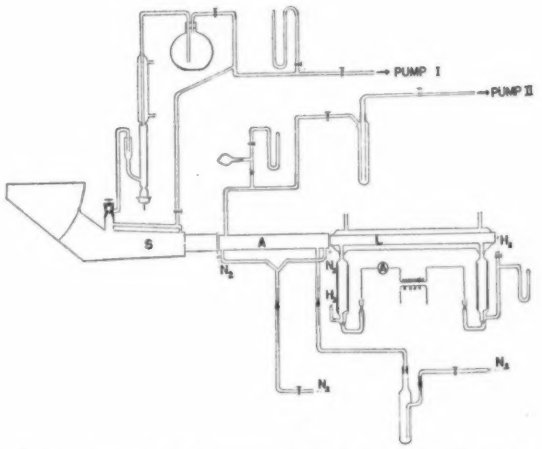


FIG. 1 shows the light source L (H_2-lamp), the absorption tube A and the spectrograph S. Nitrogen enters the vessel containing the liquid hydrocarbon through a capillary and after being saturated with the vapor is passed through another capillary into the absorption cell. A steady current of pure nitrogen flows against both fluorite windows of the cell and avoids a contact between the hydrocarbon vapor and the sealing material at the windows. The absorption tube is connected with a pump which makes possible the continuous flow of the mixture of nitrogen and vapor. The small gap between the windows of the cell, the spectrograph and the hydrogen lamp is kept free from air by a nitrogen stream under atmospheric pressure.

With the exception of three of the butenes all of the hydrocarbons studied show only diffuse absorption bands. It is possible only to measure the center of the bands and measurements on different plates may vary by 50–80 cm^{-1}. Only a few bands in each spectrum were sufficiently sharp to obtain a higher accuracy in measuring. In general, all plates were measured, but because of variations in quality of the plates as well as in the experimental conditions certain plates gave much sharper bands and the final results were taken from one plate which seemed to give the sharpest maxima. For each compound a number of plates were taken, each having 5 exposures through the hydrocarbon at different partial pressures as well as two comparison spectra of the hydrogen discharge taken before and after the hydrocarbon was photographed. In order to study the complete spectrum from 10 to 40 plates were taken for each compound examined. In the case of a number of the olefines there was a broad continuous band adjacent on the short wave side to a set of discrete bands. The maximum of this

[3] These hydrocarbons were made available for our spectroscopic work through the courtesy of Professor G. B. Kistiakowsky of Harvard University and are of the same high purity as the samples used for their hydrogenation experiments.

[4] Carr and Stücklen, Zeits. f. physik. Chemie **B25**, 57 (1934).

TABLE I.

Group I

Butene-1		Pentene-1		Heptene-1		Isopropylethylene	
λ (A)	1/λ (cm⁻¹)	λ (A)	1/λ (cm⁻¹)	λ (A)	1/λ (cm⁻¹)	λ (A)	1/λ (cm⁻¹)
1875	53330	1884	53080	1886	53020	1895	52770
1819	54970	1830	54640	1831	54610	1865	53620
1730	57800 (max. band *B*)	1740	57470 (max. band *B*)	1740	57470 (max. band *B*)	1813	55160
						1730	57800 (max. band *B*)

Group II a

cis Butene-2[1]				*trans* Butene-2[1]			
λ (A)	1/λ (cm⁻¹)	λ (A)	1/λ (cm⁻¹)	λ (A)	1/λ (cm⁻¹)	λ (A)	1/λ (cm⁻¹)
2072	48260	1924	51970	2052	48730	1917	52160
2014	49650	1889	52940	2024	49400	1894	52800
1955	51140	1869	53500	1989	50270	1750	57140 (max. band *B*)
		1740	57470 (max. band *B*)	1964	50920		

Pentene-2				Hexene-3			
λ (A)	1/λ (cm⁻¹)	λ (A)	1/λ (cm⁻¹)	λ (A)	1/λ (cm⁻¹)	λ (A)	1/λ (cm⁻¹)
2051	48760	1911	52330	2033	49190	1851	54020
2009	49780	1859	53800	1994	50150	1792	55800
1977	50580	1770	56500 (max. band *B*)	(1958)	(51070)[2]	1746	57270
1947	51360			1939	51570	1706	58620

Group II b

Isobutene[1]				Unsym. Methyl Ethyl Ethylene			
λ (A)	1/λ (cm⁻¹)	λ (A)	1/λ (cm⁻¹)	λ (A)	1/λ (cm⁻¹)	λ (A)	1/λ (cm⁻¹)
2018	49550	1792	55800	2009	49780	1785	56020
1935	51680	1776	56310	1935	51680	1730	57800
1887	52990	1747	57240	1881	53160	1690	59170
1840	54350	1705	58650	1827	54730	1657	60350
		1671	59840				

Diisobutylene I			
λ (A)	1/λ (cm⁻¹)	λ (A)	1/λ (cm⁻¹)
2035	49140	1906	52460
1965	50890	1863	53680

Group III

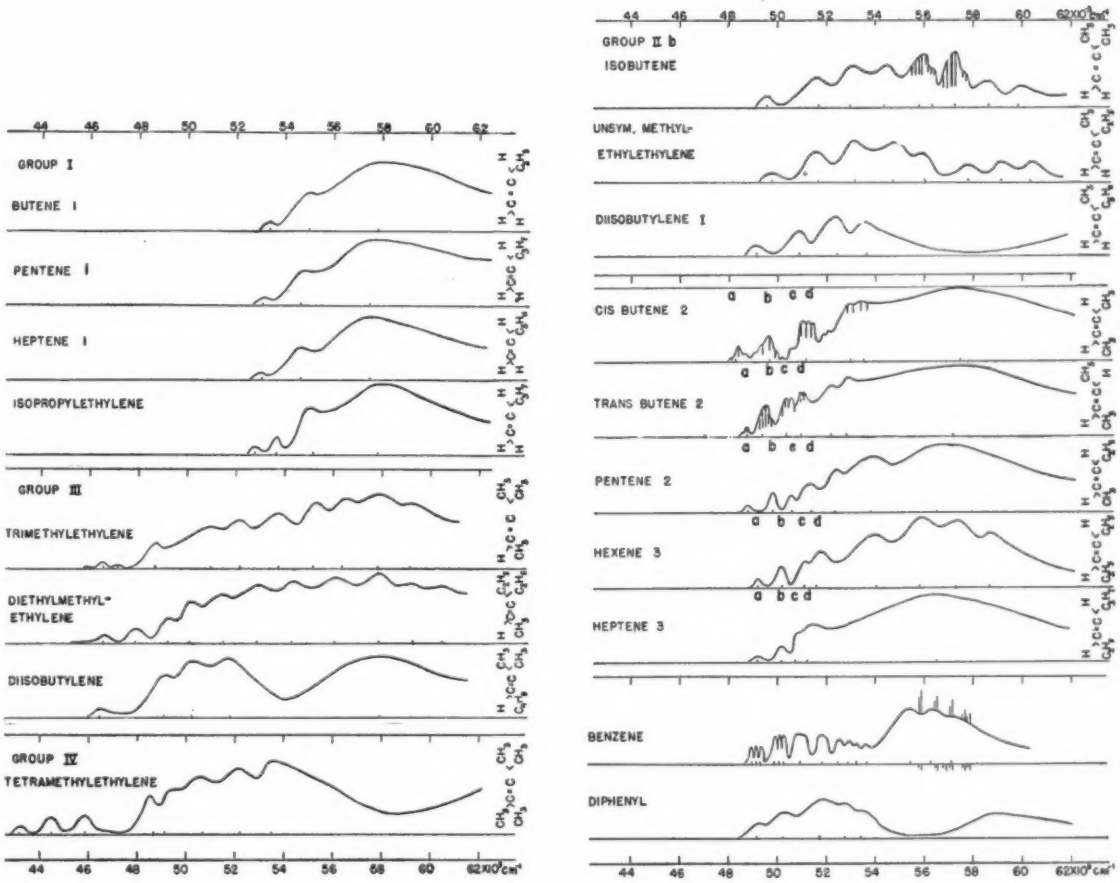
Trimethylethylene				Diethylmethylethylene			
λ (A)	1/λ (cm⁻¹)	λ (A)	1/λ (cm⁻¹)	λ (A)	1/λ (cm⁻¹)	λ (A)	1/λ (cm⁻¹)
2181	45850	1861	53730	2150	46510	1842	54290
2148	46550[3]	1812	55190	2090	47850	1785	56020
2122	47120	1774	56370	2033	49190	1729	57840
2055	48660	1729	57840	1997	50070	1688	59240
1962	50970	1691	59140	1943	51470	1655	60420
1917	52160			1893	52830		

Diisobutylene II			
λ (A)	1/λ (cm⁻¹)	λ (A)	1/λ (cm⁻¹)
2156	46380	1933	51730
2040	49020	1727	57900 (max. band *B*)
1993	50170		

[1] Some fine structure can be seen, but in this paper only the center of each group of bands is given. The analysis of the fine structure of 3 butenes will be reported later.
[2] Indicates a step-out not a discrete band.
[3] Center of a band showing threefold splitting.

band could not be determined with a greater accuracy than ±10A (±300 cm⁻¹).

The presence of even small amounts of peroxides in the hydrocarbons was found in absorption measurements in the liquid phase to be associated with a considerable shift of absorption toward the visible but no evidence of any such effect could be detected in the vapor phase measurements in the Schumann region although hydrocarbons known to contain peroxide were examined. Similarly different samples of a given hydrocarbon whose absorption spectra in hexane solution showed considerable variation in the intensity of the step-out at 42,000–45,000 cm⁻¹



FIGS. 2a AND b. Absorption bands of ethylenic derivatives. The intensities are estimated from the partial pressure of the hydrocarbon and the appearance of the bands on the photographic plate. The number of the group indicates the number of alkyl groups that are substituted for the hydrogen atoms of ethylene.

showed no detectable difference in the measurements of the vapor spectra with the fluorite spectrograph.

RESULTS

In the preceding tables (Table I) wave-lengths and wave numbers of the center of the absorption bands are given for each of the hydrocarbons studied. In the curves given in Fig. 2, the relative intensities are estimated on the basis of their appearance on the photographic plates. It should be noted that the continuous background given by the light source (H_2-lamp) diminishes toward the short wave region around 1650A where the many-line spectrum begins. Absorption bands appearing in the region where the continuous background shows decreasing intensity would probably show a somewhat different intensity, as estimated from the photographic plate, from that which would be obtained if the continuous background were of constant intensity throughout but it seems improbable that this factor would exert very great effect on the intensity estimates which have been made. In the region showing the many-line spectrum of hydrogen only strong bands can be identified. No discrete bands of the *pure* olefine (i.e., where no photochemical decomposition had taken place) were evident in this region but a decrease of intensity of the H_2-lines due to continuous absorption may be easily noted by comparison with the spectrum of the lamp alone.

In order to correlate the results of absorption measurements of all the ethylenic hydrocarbons investigated in this laboratory the curves for

tetramethylethylene and 3-heptene[5] are included in Fig. 2. Since certain similarities between the spectra of unsaturated aliphatic and aromatic hydrocarbons have been observed the curve for benzene[4] and diphenyl[6] are given.

No attempt has been made to make photometric records of the plates. Although the Hilger plates which were used were extremely good, the emulsion is too uneven to justify quantitative photometric work. The curves were drawn in such a way that if a set of bands, including the minima between the bands, have higher values on the ordinate than the maxima of another band or set of bands, then the pressure necessary to bring out these stronger bands is about 1/10 the pressure for the less intense band or bands. The ordinate on the curve would represent the logarithm of the intensity rather than the intensity itself.

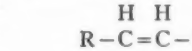
On the basis of earlier work in this laboratory a subdivision of the ultraviolet spectrum into four regions, called *A*, *B*, *C* and *D*, has been made. The region *A*, showing continuous absorption, included that portion below 1550A and was ascribed to an electronic excitation related to the saturated C−C linkage; the other three regions were correlated with the unsaturated C=C bond; region *B* on the basis of the earlier experiments consisted of a broad continuous band between 1800 and 1700A. Region *C*, between 2300 and 1800A, consisted in general of narrow, fairly discrete bands and *D* was the quartz ultraviolet part of the spectrum. In the recent much more extensive investigation the classification into the regions *A* and *D* remain unchanged, but the *B* and *C* regions are altered somewhat. The region previously designated as *B* is not always one of continuous absorption only but may have some discrete bands; also, from a theoretical standpoint as will be developed later, it seems advisable to divide region *C* into two parts, of which the region of shorter wave-length seems more closely related to the *B* region than the long wave region of *C* and will hereafter be designated as B_2 while the earlier *B* region is called B_1.

Before taking up the detailed discussion of our results it is of interest to note the general characteristics of the various spectra in relation to the molecular configuration of the hydrocarbon molecule. The spectra of all of the sixteen ethylenic hydrocarbons examined can clearly be divided into four groups depending upon the number of alkyl groups which have been substituted for the hydrogen atoms of ethylene. The most striking effect is the progressive shift toward the visible of the whole set of bands as the number of alkyl groups bound to the carbon atoms of the double bond is increased, while the effect of different alkyl groups as substituents is almost negligible.

Group I

The absorption spectrum in the Schumann region begins about 53,000 cm^{-1}, two bands were found in the straight-chain hydrocarbons and three in isopropyl ethylene, followed by a broad continuous band with its maximum around 57,000 cm^{-1}.[6a]

Group IIa



(symmetrical arrangement)

In group IIa, both the *cis* and *trans* forms of 2-butene were measured while each of the other hydrocarbons of the group consisted of a mixture of the *cis* and *trans* forms.

The absorption starts between 48,000 and 49,000 cm^{-1}, and a number of discrete bands were obtained. The general similarity between the bands in the different olefines is readily apparent although certain bands may be slightly shifted. It is of interest to note the way in which band "c" is shifted toward "d" as the molecule becomes heavier until in heptene-3 this band appears merely as a "step-out" of band "d." The maximum of absorption as with Group I lies near 57,000 cm^{-1}, and it is only in hexene-3 that dis-

[5] Carr and Walker, this issue.
[6] Unpublished work.

[6a] In isopropyl ethylene a set of bands with fine structure was found at extremely high pressures (50 mm) in the region 46,000–47,000 cm^{-1}. The existence of absorption bands of much lower intensity in this longer wave region was suspected from the absorption curve of the solution and careful search was made for them. They were obtained with three different samples of isopropyl ethylene which had been prepared by two different synthetic methods. Further experiments are in progress to see whether analogous bands could be present in other compounds of Group I or whether they are characteristic of isopropyl ethylene which in its chemical reactivity differs considerably from the other compounds of this group.

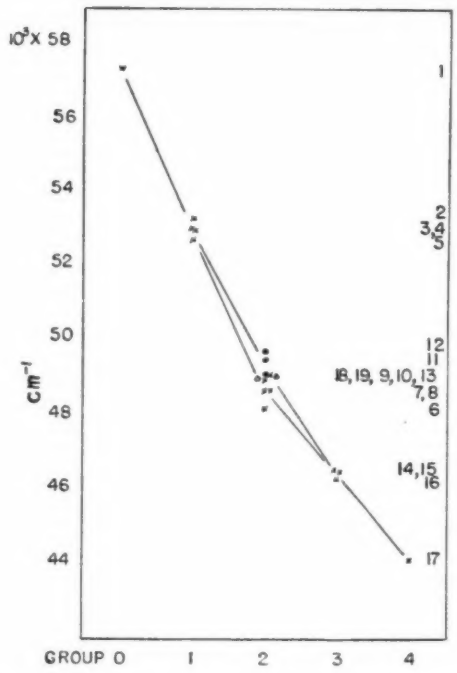


FIG. 3. Position of the first bands in the Schumann ultraviolet of ethylenic derivatives and ethylene plotted against the group number. 1, ethylene;[1] 2, butene-1; 3, pentene-1; 4, heptene-1; 5, isopropylethylene; 6, *cis* butene-2;[2] 7, *trans* butene-2;[2] 8, pentene-2; 9, hexene-3; 10, heptene-3; 11, isobutene; 12, *trans* methylethylethylene; 13, diisobutylene I; 14, trimethylethylene; 15, diethylmethylethylene; 16, diisobutylene II; 17, tetramethylethylene; 18, benzene; 19, diphenyl.

[1] Price, Phys. Rev. **47**, 451 (1935).
[2] Center of first group.

crete bands can be seen in this region. The curves for benzene and diphenyl are included for comparison with the ethylenic hydrocarbons of Group IIa since in these aromatic hydrocarbons the arrangement of hydrogen and carbon atoms around the double bond is analogous to this group and the curves show a marked similarity in the position of the first two bands.

Group IIb

$$\begin{matrix} H & R_1 \\ H-C=C-R_2 \end{matrix} \text{ (unsymmetrical)}$$

In Group IIb, where both alkyl groups are bound to the same carbon atom, the absorption begins between 49,000 and 50,000 cm^{-1}, and is thus shifted slightly to the ultraviolet in comparison with Group IIa. The most striking feature of the spectra of this group is the similarity of the first four bands in each of the compounds and the marked differences between these three compounds in the short wave region: in isobutene a set of bands with fine structure appears, in unsymmetrical methylethyl ethylene a sharp decrease in intensity occurs and in diisobutylene I the intensity diminishes to an even greater extent and shows no distinct band.

Group III

$$\begin{matrix} R_1 & H \\ R_2-C=C-R_3 \end{matrix}$$

Absorption of hydrocarbons belonging to Group III begins about 46,500 cm^{-1}, but it is much more difficult to identify analogous bands in the three hydrocarbons of this group. The sharp minimum, found in diisobutylene II at 54,000 cm^{-1}, is not found in the other compounds. With trimethylethylene there is a threefold splitting of the first band and in plotting the curve, Fig. 3, the most intense middle band is taken as the characteristic first absorption band.

Group IV

$$\begin{matrix} R & R \\ R-C=C-R \end{matrix}$$

Only one compound belonging to Group IV has been examined, tetramethylethylene. As was pointed out in the previous paper the spectrum is considerably shifted towards the red in comparison with the other hydrocarbons. The first band is at about 43,100 cm^{-1}, the maximum of absorption occurring at 53,500 cm^{-1}.

DISCUSSION

The shift of absorption in the Schumann region toward the visible as the number of alkyl groups around the double bond is increased is shown graphically in Fig. 3 where the wave number of the first band is plotted against the number of alkyl groups. The value for ethylene, as Group 0, is taken from Price's measurements.[7]

In this curve, Group II is divided into two parts, IIa with the symmetrical arrangement, $\begin{matrix} H & H \\ RC=CR \end{matrix}$, has on the average a slightly lower wave number for the first band than IIb, $\begin{matrix} R & H \\ RC=CH \end{matrix}$, the unsymmetrical arrangement. The smoothness of the curve (Fig. 3) leads to the conclusion that the electronic excitation which

[7] Price, Phys. Rev. **47**, 444 (1935).

accounts for the first absorption band in all of the olefines must be the same for all the ethylenic derivatives and closely related to that in ethylene itself. Applying the principle of the linear combination of atomic orbitals, Mulliken[8] has given an interpretation of the electronic configuration of ethylene according to which the lowest electronic state is an A_1 state and the first excitation would be of the type $[x+x]\rightarrow[x-x]$. This transition results in two excited levels, $^3B_1$ and $^1B_1$, of which the $^3B_1$ is the lower. Since the change $^1A_1\rightarrow{}^3B_1$ involves a change in multiplicity of the term, the probability of this transition was estimated to be of the order of 10^{-4} of that for the $^1A_1\rightarrow{}^1B_1$ transition.

Snow and Allsopp[9] have applied a similar process of reasoning to the C=C double bond in ethylenic derivatives, assuming the ground state of $R_1R_2C=CR_3R_4$ to be a $^1A_1$ level. Since for molecules of lower symmetry the number of upper states which are permitted is greater, it is possible, as was pointed out by Snow and Allsopp, that the absorption spectrum of ethylenic derivatives may be quite different from that of ethylene. Their study, however, of the spectra of trimethylethylene, cyclohexene and ethylene indicated a marked similarity between the upper states of ethylene and of ethylene derivatives and on the basis of their results a tentative assignment of the weak bands of cyclohexene and trimethylethylene measured in liquid and solution phase in the long wave region was made as due to the transition $^1A_1\rightarrow{}^3B_1$, whereas the much more intense bands in the region 2160–2080A were tentatively assigned to a $^1A_1\rightarrow{}^1B_1$ transition.

Largely because of the analogous structure of the bands observed in the spectra of ethylene and its derivatives, Snow and Allsopp concluded that the band system of ethylene derivatives at about 2100A is the same in origin as the group of bands in ethylene at slightly shorter wave-lengths (2069 to 1935A) although the discrepancy in intensities seemed puzzling since the bands for the derivatives have intensities 100 times as great as the bands which they considered to be the corresponding bands of ethylene. On the basis of our results as shown by the curve it would seem more probable that the band system of ethylene which corresponds to the bands of the derivatives in the 2100A region is that observed by Price[7] as beginning at 1744A (57,320 cm^{-1}). Such a conclusion has further justification when one compares the difference in wave numbers between the beginning of absorption in the low intensity band of the liquid hydrocarbon and the first band of that compound in the Schumann region. As was pointed out in the preceding paper of this series the beginning of absorption in the quartz region as measured by the frequency corresponding to $\log\epsilon=-2.00$, is shifted progressively towards the visible with increasing number of alkyl groups attached to the carbon atoms of the double bond in the same way in which the first band in the Schumann region spectra is displaced. For the twelve hydrocarbons which were measured in both quartz and Schumann regions, the difference in wave-numbers is between 12,850 and 15,000 cm^{-1}. The difference for ethylene is 14,300 cm^{-1} if 1744A is compared with 2325A for $\log\epsilon=-2.00$, which is obtained from a short extrapolation of Snow and Allsopp's curve for liquid ethylene.

The matter of relative intensities for such an assignment of corresponding bands of ethylene and its derivatives would seem to be more consistent. Although our intensity estimates in the vapor phase measurements are only approximate it was found that for all the ethylenic derivatives a partial pressure of somewhat less than 1 mm is necessary to bring out the first band, thus indicating a close parallelism in the intensities of corresponding bands. The intensity of the ethylene band at 1744A, according to the measurements of Scheibe and Grieneisen[10] must be of the same order since this band appears when the partial pressure of the ethylene is between 1 mm and 0.1 mm.

If Snow and Allsopp's assignment of $^1A_1\rightarrow{}^1B_1$ for the bands of ethylene derivatives in the 2100A region is correct then the first band found by Price for ethylene should be assigned to the same transition. Similarly the absorption of ethylene in the quartz region beginning about 2300A would be assigned to a $^1A_1\rightarrow{}^3B_1$ transition. The parallelism which is evident between the shift of

[8] Mulliken, Phys. Rev. **41**, 751 (1932); J. Chem. Phys. **3**, 517 (1935).
[9] Snow and Allsopp, Trans. Faraday Soc. **30**, 93 (1934).
[10] Scheibe and Grieneisen, Zeits. f. physik. Chemie **B25**, 52 (1934).

absorption in the quartz region and in the Schumann region when the configuration of the molecule is altered indicates a close relationship between the electronic transitions concerned and gives strong support to the correctness of Snow and Allsopp's assignment of levels for the ethylenic derivatives.

The sphere of influence of the $[x+x]$ and $[x-x]$ orbitals is localized in the neighborhood of the C=C bond according to Mulliken, and would therefore be little influenced by varying the alkyl group attached to the carbon atom and consequently the position of the first band would be independent of the nature of the alkyl group. The progressive shift toward the visible with increasing number of alkyl groups should be considered from the point of view of the decrease in the number of hydrogen atoms bound to the carbon atoms of the double bond and the consequent effect on the carbon atom or rather the $[x]$ orbitals due to the replacement of hydrogen atoms by the less electropositive alkyl groups. From this point of view a comparison of the ionization potentials of ethylenic derivatives having different numbers of alkyl groups around the double bond would be of interest. The fact that the position of the first band in the spectrum of benzene, as well as of diphenyl, should bring these hydrocarbons in Group IIa of the olefine classification seems to be more than an accidental coincidence and to imply that the relationship is of fundamental significance in the interpretation of the energy relationships of unsaturated hydrocarbons.

Although the nature of the alkyl substituent has only a very slight effect it is of interest to note that the experimental points which show the greatest deviation from the curve are those in which the alkyl groups have a branched chain which would indicate that there is a slight influence due to spatial configuration.

Fig. 2 indicates that after the first or the first few bands the intensity of absorption increases sharply. This rise in intensity is such that the partial pressure of the hydrocarbon must be decreased to one-tenth or less of its previous pressure to bring out the next set of bands on the photographic plate. In some cases there is a remarkably large gap between the last band of low intensity (region *C*) and the first of the high intensity group. This change in intensity is so marked in all of the hydrocarbons that it would seem to represent a transition to another upper level and this group of bands, which was included in region *C* in the earlier paper[4] has now been considered as belonging to Group *B*. Although this transition is characteristic of all the olefines, the point at which this band system appears varies with the different hydrocarbons and the bands overlap those of region *C* to such an extent that it is not possible to follow the vibrational spectrum in either group. It is perhaps premature to assign a definite transition to this group of bands but it seems probable that it is a transition which is restricted to molecules of lower symmetry than ethylene since neither Price nor Scheibe and Grieneisen report a corresponding group of bands in ethylene.

The character of the spectrum of certain olefines indicates that a subdivision should be made within the region designated as *B*. This shows most clearly in Group IIb, where there is a sharp change in the spectrum beginning about 55,000 cm^{-1}. In isobutene this change is marked by the appearance of bands with fine structure, in unsymmetrical methylethylethylene and diisobutylene I, by the sharp decrease in intensity. In diisobutylene II, a similar decrease in intensity is apparent and is followed by another band. This region which in these four compounds begins about 55,000 cm^{-1} has been designated as region B_1, and the region of longer wave-length as B_2. Whether the same subdivision is justified for the other olefines and where it should be made is uncertain, both regions may overlap to such an extent that no separation is apparent. It is of interest to note, however, that the subdivision shows most clearly in those compounds where there is unsymmetrical substitution of hydrogen atoms of ethylene. The group of bands designated as belonging to region B_1 indicates another electronic transition which like B_2 seems to have no counterpart, at least of comparable intensity in the spectrum of ethylene.

With regard to the vibrational spectra of the ethylene compounds there are certain general relationships which are of interest but no detailed analysis is possible because of the breadth and diffuseness of the bands. In the case of the three butenes in which only two methyl groups are

bound to the C=C nucleus, the single vibrations are resolved and the analysis of these spectra will be considered in a separate paper. An excitation of an electron in an $[x]$ orbital, localized in the region of the C=C bond would have little if any influence on the rest of the molecule and as a consequence the number of vibrational frequencies associated with this electronic excitation is limited. In the case of ethylene, Price reports only two different types of vibration with frequencies of 1340 and 480 cm^{-1} associated with the first electronic band and these vibrations were believed to depend mainly on the C=C linking whereas the vibrations which involve the C−H bonds are not excited. In the ethylene derivatives, some fairly constant frequency differences are evident in region *C*; for example, about 1350 cm^{-1} between the first bands of tetramethylethylene and between the first two of diethylmethylethylene, but in general only one member of a series can be found in region *C*.

In regions B_2 and B_1 such restrictions do not seem to hold since a considerable number of band maxima may be seen although the bands are less sharp and more difficult to distinguish than in region *C*. Fig. 2 shows that although there is no consistent frequency difference between adjacent band maxima yet in most cases the separation of these maxima lies between 1200 and 1500 cm^{-1}. If the strongest vibration which occurs in all these molecules is one along the C=C axis and this frequency is of the same order as that in ethylene, 1350 cm^{-1}, it is quite possible that this vibration is combined with deformation vibrations of smaller frequency and lower intensity. Since the *B* region is one of strong predissociation, the single vibrations give rise to fairly broad bands and these broad bands coalesce in such a way as to result in a maximum of absorption which is more or less shifted in relation to any single vibration. The maximum is therefore rather an accidental one which shows only an approximate relationship to the strongest of the excited vibrations. In bands c and d of Group IIa it is possible to follow the way in which two band maxima merge into each other as the weight of the molecule increases.

It is of interest to note that in hexene-3 and in tetramethylethylene a greater number of bands can be seen than in the more unsymmetrical molecules although the contrary would be expected from the selection rules. This must be due to the fact that with the more symmetrical molecules fewer vibrations are excited and consequently there is less overlapping and the bands show more clearly.

The intensity distribution of vibrational sequences is puzzling. A maximum of absorption is reached at the point at which the broad continuous band has its maximum, at about 57,000 cm^{-1}, but there is no evidence of a strongly absorbing 0−0 band nor of decreasing intensity of band maxima in a vibrational sequence. If the probability of transition to the B_1 and B_2 levels were very nearly the same, the absorption would overlap and thus explain in part the intensity increase toward the maximum at 57,000 cm^{-1}.

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The Infrared Absorption Spectra of Dioxane-Water Mixtures

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The absorption spectra of various dioxane-water mixtures have been studied in the region 2.5μ to 6.5μ. Dioxane was found to produce marked changes in the water spectrum. The observed variations are more pronounced for low water concentrations. Association of the water and dioxane molecules is suggested as a possible explanation of the observed effects.

THE fact that dioxane is completely miscible with water and the additional fact that dioxane has a very low dielectric constant as compared to water, makes dioxane-water mixtures very advantageous in chemical investigations.[1] These properties suggest the study of variations in the electric moment, as evidenced by changes in the infrared absorption spectra, of the water molecules when mixed in various proportions with dioxane. Since dioxane is almost, if not completely, nonpolar, the electric moment of the water dissolved in dioxane may be expected to approach that of the vapor-like state as the water concentration is lowered. Spectroscopic evidence for the existence of vapor-like molecules of water dissolved in carbon disulfide has been given by Kinsey and Ellis.[2] Their work has been reported only for the region 1.0μ to 2.5μ. On the other hand, there may be a linkage between the dioxane and water molecules, resulting in changes of the electric moment and hence variations in the absorption spectra of the water. In addition, associational bands may appear. Infrared absorption evidence of associational effects in acetone-water mixtures[3] and in alcohol-water mixtures[4] has been reported. Akerlof and Short[1] have measured the dielectric constant of mixtures of dioxane and water and have computed the polarization of each for various concentrations. They found the apparent polarization of the water to increase linearly as the dioxane content in the solution was increased.

The experimental method has been previously described.[5] A fluorite prism was used for the entire region studied. Cell windows were of fluorite and were sealed with paraffin. The absorbing layer was maintained at a constant thickness of 0.002 cm. The dioxane was dried for four days over sodium. Cell windows were dried over P_2O_5.

A careful study has been made of the water bands in the 3μ, 4.7μ, and the 6.18μ regions for various dioxane-water mixtures. Results for the 3μ region are given in Fig. 1. The bottom curve represents the transmission of pure water. The center of the water band appears at approximately 3μ. It will be seen from the next curve, which represents the transmission of a dioxane-water mixture of 50 percent water, that the 3μ water band has been shifted to the shorter wave-lengths. As the water concentration is decreased to 13 percent, to 7 percent and to 4 percent, the position of maximum absorption continues to shift to the shorter wave-lengths. For 4 percent water solution the band appears at 2.8μ, having been shifted approximately 0.2μ. Results obtained for 2 percent and 0.5 percent concentrations are not given in the figure. For concentrations below 4 percent the shift apparently remains constant. The band, however, is still strong for concentrations as low as 0.5 percent. This suggests the possibility of using this band for purposes of detecting small traces of water in samples of dioxane. In addition to the shift in position there is an increase in intensity of the 3μ band as the water content in the mixture is decreased. The intensity of the band does not decrease in proportion to the decrease in the number of absorbers. The curve for the supposedly anhydrous dioxane shows a small band in the 2.8μ region. It is likely that

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[1] C. A. Kraus and R. M. Fuoss, J. Am. Chem. Soc. **55**, 21 (1933); G. Akerlof and O. A. Short, J. Am. Chem. Soc. **58**, 1241 (1936).

[2] E. L. Kinsey and J. W. Ellis, Phys. Rev. **49**, 105 (1936).

[3] D. Williams and E. K. Plyler, J. Chem. Phys. **4**, 157 (1936).

[4] D. Williams, R. D. Weatherford and E. K. Plyler, J. Opt. Soc. Am. **26**, 149 (1936).

[5] W. Gordy and D. Williams, J. Chem. Phys. **3**, 664 (1935).

this absorption is due to traces of water that could not be removed or that was taken in from the air as the cell was being made. The strong band at 3.38μ in dioxane spectrum appears to remain constant in position as the dioxane concentration is varied. Because of the intense absorption of water it was not possible to study this band for low dioxane concentrations.

The 4.7μ water band is of particular interest in this study because there is no corresponding band in the vapor state. Its origin has been attributed to association between the water molecules.[6] This band could not be observed in dioxane-water mixtures for water concentrations as low as 7 percent. It definitely appears, however, in the 13 percent mixtures. The absorption curves for the region 4.4μ to 5.2μ for 7 and 13 percent mixtures with those of pure water are given in Fig. 2. The band appearing at 5.05μ, characteristic of the dioxane, was not measurably affected by the water for the concentrations studied.

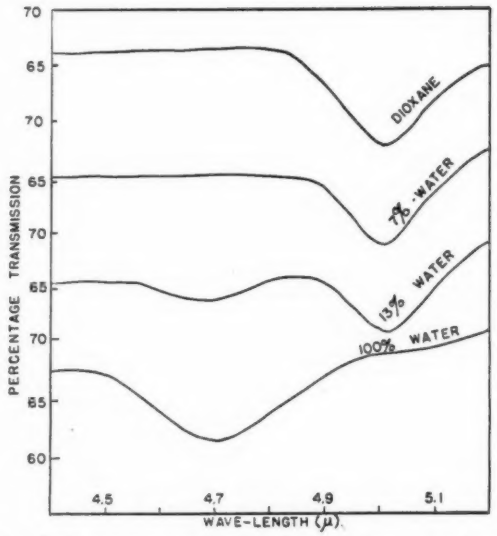

FIG. 2. The percentage transmission of dioxane and water and dioxane-water mixtures in the region 4.4μ to 5.2μ. The mixtures are given in percentage by volume.

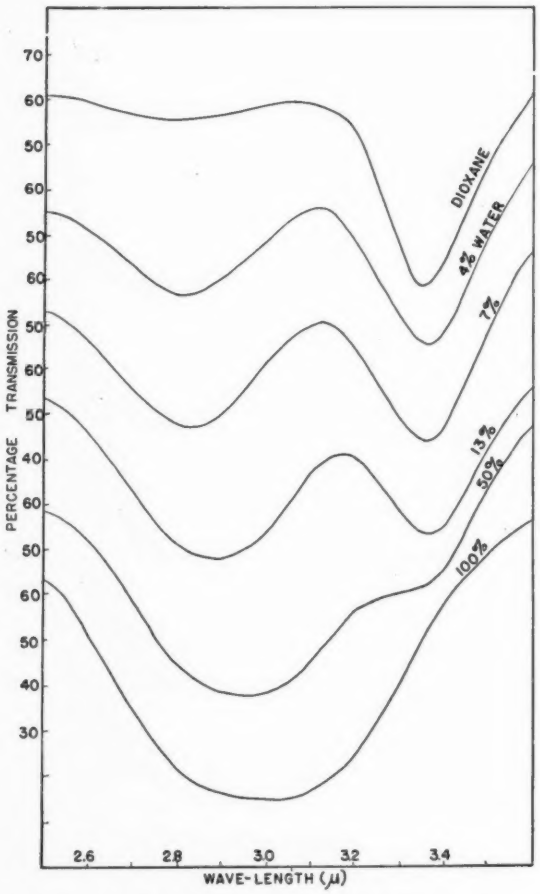

FIG. 1. The percentage transmission of dioxane and water and dioxane-water mixtures in the region 2.5μ to 3.6μ. The mixtures are given in percentage by volume.

[6] J. W. Ellis, Phys. Rev. **38**, 693 (1931).

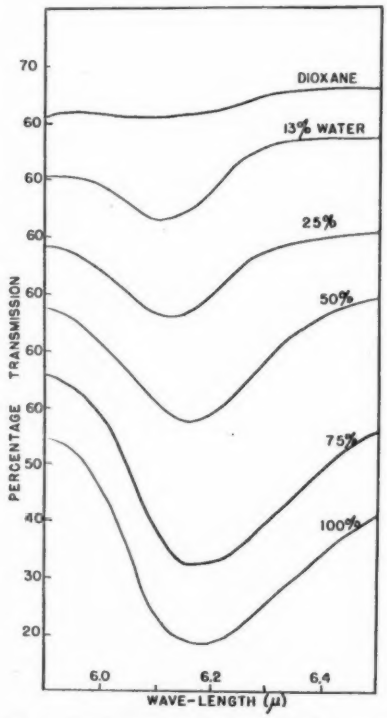

FIG. 3. The percentage transmission of dioxane and water and dioxane-water mixtures in the region 5.9μ to 6.5μ. The mixtures are given in percentage by volume.

In Fig. 3 are given the results obtained for the region 5.9μ to 6.5μ. The mixtures vary in concentration of water from 13 to 75 percent. It is obvious from the figure that the water band is shifted to the shorter wave-lengths as the dioxane content is increased. The intensity of the band is not increased appreciably as was the case of the 3μ band. The magnitude of the shift is about half that of the 3μ band.

Theoretical curves were developed for the 3μ and 6μ regions on the assumption that the absorption coefficient of the mixture at any wave-length is equal to the mean of the absorption coefficients of the two components at the same wave-lengths. The method of computation has been explained by Williams and Plyler.[3] In Figs. 4 and 5 these curves are shown in comparison with the experimental curves for the same mixtures. The marked differences in the experimental and theoretical transmission in these regions show clearly that the effects observed cannot be due to the supposition of water and dioxane bands.

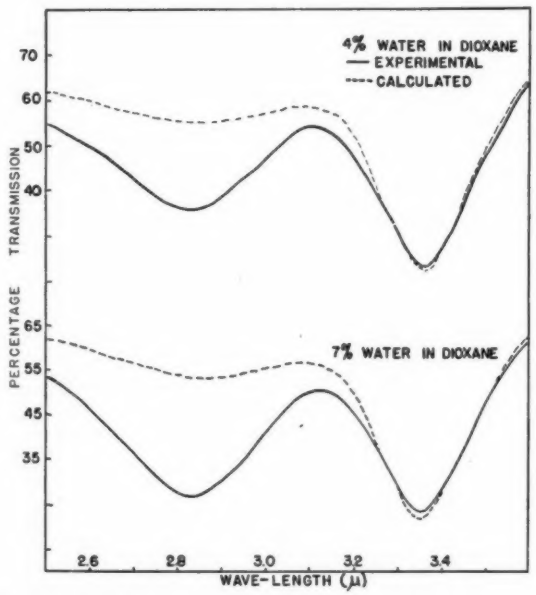

FIG. 4. The theoretical and experimental transmission of the dioxane-water mixtures in the region 2.5μ to 3.6μ.

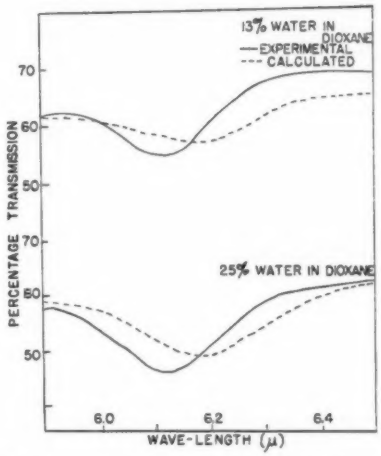

FIG. 5. The theoretical and experimental transmission of the dioxane-water mixtures in the region 5.9μ to 6.5μ.

Water vapor has strong absorption bands at 2.66μ and at 2.74μ. One might interpret the shift observed in the 3μ water band as a transition of the water absorption to vapor-like absorption. The disappearance of the 4.7μ water band for low concentrations supports this hypothesis. The changes observed in the 6μ region, however, fail to support the assumption that the effects observed are due to vapor-like molecules in the solution. From the behavior of the 4.7μ band, it seems likely that there is a separation of the associated molecules as the water concentration is decreased. The changes in the 3μ and 6.18μ water bands are probably due to association between the water and dioxane molecules. A possible explanation of the association would be the "proton bond" theory.[7] If the dioxane and water molecules are linked through a hydrogen bond, we should expect the electric moment of the group which carries the hydrogen to be increased. This would account for the pronounced changes observed in the water spectrum.

The writer is grateful to Dr. E. K. Plyler for the use of his instrument.

[7] W. M. Latimer and W. H. Rodebush, J. Am. Chem. Soc. **42**, 1419 (1920); L. Pauling, J. Am. Chem. Soc. **57**, 2680 (1935); ibid. **58**, 94 (1936).

Vibration Spectra and Molecular Structure

I. General Remarks and a Study of the Spectrum of the OH Group

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A brief survey is given of the ideas underlying the interpretation of molecular vibration spectra in connection with molecular structure problems. This is followed by a discussion of the reasons for the appearance or nonappearance in the spectrum of the characteristic frequency at 3400 cm^{-1} for various molecules containing the OH group. In certain alcohols and glycols this frequency has not been reported in the Raman effect, but it is concluded that this must be due to experimental difficulties. In the carboxylic acids, on the other hand, as well as in certain aromatic compounds containing OH, the characteristic frequency is definitely absent from both the Raman and infrared spectra, and the role of the hydrogen bond in association and chelation is discussed in connection with these cases.

INTRODUCTION

STUDY of molecular structure by means of infrared and Raman spectra has progressed in two directions. One attack may be said to derive from the highly developed subject of diatomic molecular spectroscopy. Here triatomic molecules and the simpler molecules of four, five and six atoms are studied with high resolution and carefully analyzed in terms of accurate solutions of the complicated vibration problems involved. Progress in this direction is necessarily slow and beset with many difficulties.

Another attack corresponds to the one which has received attention for many years—the semi-quantitative, half-empirical correlation of observed frequencies to individual valence bonds in the molecule. In spite of the vast amount of work that has been put on this side of the subject we believe that there is still a great deal to be learned about molecular structure by a critical discussion of the data in terms of these less precise methods. Not only can many questions of molecular structure be answered in this way now, but a careful study of the empirical material from this standpoint will be a necessary preliminary to the extension of precision methods to complicated molecules. Therefore it is our intention in the series of papers of which this is the first, to make a careful survey of the empirical material in terms of the simpler methods of interpretation.

This paper includes a survey of the general ideas used and a discussion of factors affecting the appearance of the band due to the hydroxyl group in various compounds.

Valence bond frequencies

A well-known fact of infrared spectroscopy and of its lusty nephew, Raman spectroscopy, is that certain frequencies can be correlated closely with the occurrence in the molecule of certain valence bonds. Curiously enough such correlations are often more constant and uniform in complicated molecules, the notable departures occurring in the lowest members of homologous series. This is connected with the fact that symmetry restrictions usually affect the simpler molecules while in more complicated structures the symmetry elements are lost. Also, in a series of complex molecules the environment of a given bond is more likely to be constant.

If the situation were so simple that there would always be associated a vibration frequency with each type of bond in the molecule, then obviously the molecular vibration method of analysis would provide a very powerful means of investigating the structures of molecules. The situation is in fact almost that simple and a large part of the spectrum in the fundamental vibration region is understandable at a glance. In a recent paper by one of us[1] there is given a brief survey of the type of problem to which these methods are applicable, and of the mode of attack used in some cases. Suffice it to say that important informa-

* Now with the American Cyanamid Company.
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[1] R. B. Barnes, Rev. Sci. Inst. **7**, 265 (1936).

tion has already been obtained in the fields of deuterochemistry, polymerization, isomerism, chelation, and many others and that the possible extensions in these and other fields appear to be almost unlimited. In the present paper we wish to point out that exceptions to the principle of constant bond frequencies frequently occur, and that from these exceptions information is obtained which is just as valuable as that obtained from the regularities. When such exceptions occur it is often possible to give a simple dynamical explanation in terms of the vibration forms of the molecule. If such an explanation is not possible it can frequently be shown that the classical structural formula of the molecule under investigation is not entirely correct.

As regards the dynamical effects mentioned above, it should be pointed out that it is the bond force constant and not the position of the infrared absorption or Raman frequency that is characteristic of the specific bond. Therefore a knowledge of these bond force constants is essential if the effects on the positions of the molecular frequencies caused by such phenomena as the interaction between two neighboring similar bonds is to be correctly explained. For this reason frequent reference will be made in what follows to the values of these constants and to the methods used in their calculation.

Following the ideas of Mecke, Dennison, Sutherland and others[2–4] we suppose the principal forces involved are those of a valence force system, namely forces between those atoms which are chemically bonded, obeying Hooke's law for small displacements from equilibrium, and a system of torques tending to preserve the bond angles at the tetrahedral value for carbon and at the appropriate other angles for other polyvalent atoms. In the more accurate analyses other terms are inserted to represent interaction forces between different valence bonds but their effects are usually small.

The next point to make is that accurate analysis of simpler cases has shown the forces preserving valence angles to be much weaker than those available for preserving bond distances. This fact together with the fact that "straight-chain" compounds are actually zigzag in form tends to reduce the amount of dynamical interaction between different valence bond oscillations, as was pointed out by Bartholomé and Teller[5] and recently by Bauermeister and Weizel.[6] Because of the weakness of the directed valence forces those frequencies in which angles vary are generally lower in value than the valence oscillations, being generally less than 1000 cm^{-1}. Also as a result of this weakness the deformation frequencies are affected more strongly by neighboring atoms or groups and do not show such simple empirical regularities as the valence oscillations. They will, therefore, receive almost no consideration in what follows.

To the approximation that Hooke's law forces are obeyed, every theoretical formula relating a vibration frequency to the force constants and masses in a molecule will have a dimensional similarity with that for the simple harmonic oscillator,

$$\tilde{\nu} = (2\pi c)^{-1}(k/m)^{\frac{1}{2}}. \tag{1}$$

Here $\tilde{\nu}$ is the frequency in cm^{-1}, m is the mass and k is the force constant in the equation connecting potential energy, V and displacement x from the equilibrium position,

$$V = \tfrac{1}{2}kx^2. \tag{2}$$

It is convenient to standardize the units, once and for all. All known values of the force constant are of the order of 10^5 dyne/cm so we shall adopt this as a convenient unit for k. We have:

$$\begin{aligned} 10^5 \text{ dyne/cm} &= 10^5 \text{ erg/cm}^2 = 6.284\, eV/\text{A}^2 \\ &= 509.5 \text{ cm}^{-1}/(10^{-9} \text{ cm})^2 \\ &= 1.449 \text{ (cal/mole)}/(10^{-9} \text{ cm})^2, \end{aligned} \tag{3}$$

which enables conversions of k to other energy and length units to be readily made. For the masses it is convenient to use atomic weights on the oxygen = 16 scale. Using Birge's values for the universal constants the formula that is the dimensional model for all normal modes solutions of vibration problems becomes

$$\tilde{\nu} = 1307\ (k/m)^{\frac{1}{2}}. \tag{1'}$$

We turn now to a rapid survey of the funda-

[2] R. Mecke, Zeits. f. physik. Chemie **B16**, 409, 421; **B17**, 1 (1932).
[3] D. M. Dennison, Rev. Mod. Phys. **3**, 280 (1931).
[4] Sutherland and Dennison, Proc. Roy. Soc. **A148**, 250 (1935).
[5] Bartholomé and Teller, Zeits. f. physik. Chemie **B19**, 366 (1932).
[6] Bauermeister and Weizel, Physik. Zeits. **37**, 169 (1936).

mental frequencies and force constants characteristic of bonds of the type commonly occurring in organic molecules.

Single bonds with hydrogen: CH, OH, NH, SH

Nearly every molecule considered contains one or more CH bonds. All such show infrared absorption and Raman lines between 2600 and 3050 cm^{-1}, the strongest frequencies in aliphatic molecules being generally close to 2900. In aromatic molecules the frequency is generally higher being near 3050 as a rule. The simplest view of the matter is to suppose the CH bonds capable of vibration pretty much as independent units in spite of their being part of the larger structure. To that approximation the frequency is given by (1).

With increasing complexity of structure the number of frequencies attributable to CH increases. Here, however, the emphasis is on the comparatively narrow range of these frequencies. The frequency 2918 in methane corresponds to symmetric contraction-expansion of the tetrahedron: here the carbon stands still and the four hydrogen atoms move with alteration of the four bond distances. The frequency may be calculated from (1′) with $m=1$, and k the constant for the CH bond. This yields a value of $k=5.00$ which agrees well with the value 5.02 obtained by Bonner[7] from a detailed analysis for ethylene. For further comparison we note that the frequency in the normal electronic state of CH in the diatomic band system is 2859, which together with the reduced mass value 0.924 gives 4.44 for k. Provisionally we postulate that k has the value 5.00 for all organic CH bonds.

Characteristic of all compounds containing the OH group is a frequency close to 3400. Since this group has many interesting special properties and since there is a good deal of confusion about it in the literature it is dealt with in detail in the latter part of this paper. In diatomic OH from electronic bands, the normal state frequency is 3735 corresponding to $k=7.72$ while in H_2O vapor the two normal modes which are essentially valence oscillations are 3600 and 3756, and the force constant for OH found in Bonner's[8] analysis of the water spectrum is 8.233. The value obtained from 3400 assuming the H to be vibrating against a large mass (reduced mass = 1) is $k=6.8$.

Frequencies characteristic of the NH bond are not greatly different from those for OH, being in the region around 3300. Here the force constant from the diatomic frequency is 5.22 while that calculated from the frequency 3320 using for the reduced mass $\mu=1$ is 6.4.

These three commonest types of bonds involving hydrogen have therefore frequencies in the range from 2800 to 3400 and may give rise to some overlapping in infrared studies with low dispersion, as with a single prism rocksalt instrument. Nevertheless it is often possible to distinguish between the bands due to these bonds as will appear later.

Characteristic of SH is a remarkably constant frequency which stays between 2570 and 2580 in the mercaptans. This is a convenient location as it happens that there are usually no other bands in this immediate neighborhood. This frequency corresponds to the much weaker force constant $k=3.85$.

Single bonds: C−C, C−O, C−N

After CH, the CC linkage occurs most frequently in organic chemistry. For the single bond CC linkage the general range of frequencies is 800 to 1150. Here there is a tendency to develop a fairly open structure of increasing complexity with growing length of carbon chain. This interaction splitting continues as the length of the chain increases, and leads to the often observed differences between the spectra of the first and higher members of homologous series. This effect has been treated recently by Bauermeister and Weizel.[6]

In ethane, for example, we find a single CC frequency at 993, whereas in propane we find two frequencies characteristic of this bond, one at 867 and the other at 1055. This splitting is an example of the type of dynamical interaction mentioned above, resulting from the presence in the molecule of adjacent similar bonds. Further examples are found in the spectra of the C−O−C and the C=C=C groups.

At this point it is perhaps timely to say a few words concerning a useful approximate method of force constant calculation introduced by Mecke,[2] and used with considerable success by him and by

[7] L. G. Bonner, J. Am. Chem. Soc. **58**, 34 (1936).
[8] L. G. Bonner, Phys. Rev. **46**, 458 (1934).

Sutherland and Dennison.[4] Since the hydrogen atoms, which are found on practically all molecules investigated to date, are very light, and their vibration frequencies as have been shown are high compared with those of neighboring groups of heavier atoms, it is frequently possible to neglect the effect of these hydrogens and to treat the groups containing hydrogen as rigid bodies. To this approximation, ethane would be treated as a diatomic molecule, each body being of mass 15, while propane would be triatomic, with two mass 15 bodies and one of mass 14. The applications and limitations of this rigid group approximation will be illustrated for a few cases in what follows, and will be taken up in considerable detail in later papers of this series. As an example of such a simplified calculation, ethane with a reduced mass of 7.5 yields a force constant $k=4.32$, which is an entirely reasonable value.

The single bond CO frequency is not always recognizable since it is so close to the single bond CC frequency. However, in methyl alcohol the frequency 1030 is readily associated with this vibration. Regarding it as a vibration of OH against CH_3 this gives $k=4.96$ for the CO force constant.

Since what has been said above illustrates well the behavior of bond frequencies and the approximate constancy of the force constants deduced therefrom, we feel it to be unnecessary to discuss further cases in detail. At this point we shall point out simply the ranges of the frequencies and force constants associated with some of the remaining principal bond types. For a detailed compilation of the frequency values the reader is referred to standard works, such as those of Schaeffer and Matossi,[9] Kohlrausch[10] and Hibben.[11]

To repeat, for purposes of comparison, the single bond values given above, we find that, for single bonds between light atoms the frequencies all lie in the range 800–1150 cm^{-1} and the force constants between 4 and 5 (in units of 10^5 dynes/cm). Double bond frequencies are generally between 1500 and 1800 corresponding to a force constant in the neighborhood of 10–12. The triple bond, again, is still higher, ranging from 1900–2300, with a force constant range of 15–20. In the methyl halides frequencies probably to be associated with the C–Cl, C–Br, and C–I bonds are found at 710, 600, and 530, respectively. It must be emphasized that these values apply principally to the aliphatic or open chain compounds and may differ appreciably from the frequencies for the same combinations existing in ring structures.

It is hoped that with this brief introduction we have made clear the empirical background underlying these studies and have outlined the aims, methods and terminology of these papers.

The Spectrum of the OH Group

Since the assumptions implied above are that any molecule containing an OH group will have a frequency in the neighborhood of 3400 cm^{-1} and since many molecules which are known, by chemical evidence, to have such a group do not exhibit this frequency, one must look for an explanation of this apparent anomaly. In what follows we propose to point out some of the principal exceptions to this rule of constant bond frequencies and to draw attention to some of the factors that may lead to the disappearance of this frequency.

Raman effect

Careful study of the original literature and of the reviews mentioned above reveals the remarkable fact that throughout the period of development through which the Raman effect has passed since its discovery in 1928 the overwhelming majority of observers failed consistently to record frequencies in the 3400 region. In view of the fact that the strong band which occurs in the infrared spectra of all alcohols at about 2.9μ (3400 cm^{-1}) has, since the days of Julius and Aschkinass been identified with the internal vibration of the OH group, it is extremely surprising that this Raman frequency should continue to be conspicuous by its absence. On page 17 of his review, Hibben states, with regard to the 3400 shift, "Unfortunately . . . this can only be detected in less than half the alcohols studied." On page 20 one sees that neither propylene glycol, glycerol nor glucose shows an OH frequency at 3400, if the list of frequencies reported is to be taken as complete.

[9] Schaeffer and Matossi, *Das Ultrarote Spektrum*.
[10] Kohlrausch, *Der Smekal Raman Effekt*.
[11] J. H. Hibben, Chem. Rev. **18**, 1 (1936).

Wood and Collins[12] recently reported Raman measurements upon a beautifully complete series of eleven normal alcohols but failed to record any frequency higher than 3000. Venkateswaran and Bhagavantam[13] presented an extensive table of frequencies observed for alcohols; none, however, higher than 3000 cm^{-1}. In a footnote they remarked that "The Raman spectrum of methyl alcohol shows, besides the lines given, . . . a prominent broad band corresponding to a shift of about 3μ. . . ." The implication is that the remaining alcohols did not contain even this broad band. So it is with numerous other observers and in the cases of many other compounds containing OH. In view of the fact that all of the compounds herein mentioned do exhibit strong OH absorption in the infrared, as shown in part in curves 1–5 of the figure, and since most of them are reasonably complex molecules so that the possibility of the corresponding Raman frequencies being forbidden by selection rules based on symmetry is very small, the absence of these frequencies is puzzling. Recent Raman measurements in this laboratory have indicated the presence of the weak broad band at about 3400 cm^{-1} characteristic of the OH group, in two of the compounds mentioned above, namely propylene glycol and glycerol. As a result it is clear that caution must be used in basing analyses of the type mentioned in the introduction solely on the results of Raman measurements. The authors have found that a good general principle to be applied in the interpretation of Raman results is that, although the appearance of a line is definite, the nonappearance may be due to any one of a number of factors and does not necessarily indicate that the frequency is absent in the molecule.

Infrared

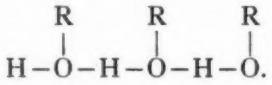
As already mentioned, all the alcohols heretofore measured have shown a strong OH absorption in the infrared, and, in fact, practically all compounds containing OH exhibit this band. There are, however, a few cases in which this absorption is definitely absent, and it is to these that we shall turn our attention.

[12] Wood and Collins, Phys. Rev. **42**, 386 (1932).
[13] Venkateswaran and Bhagavantam, Ind. J. Phys. **5**, 129 (1930).

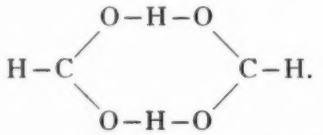
Molecules containing the carboxyl group

Sappenfield,[14] Eichmann,[15] Roth,[16] and Errera and Mollet[17] have all reported on infrared absorption of the fatty acid series, and are all in agreement that the overtones of the 3400 frequency are missing in the lower members. In addition measurements in this laboratory on formic, acetic, propionic and valeric acids in the fundamental region show that this frequency is missing for the lower members and appears only very weakly for some of the higher members of the series. This effect is exemplified by curves 6 and 7 of the figure.

The fatty acids are in general highly associated, some fifty percent of the molecules of the lower members existing as dimers even in the vapor state at an elevated temperature, according to Drucker and Ullmann.[18] This gives us the explanation for the disappearance of this band. According to Sidgwick,[19] this association takes place through the OH group of each interacting molecule, as given by the structural formula



Pauling and Brockway,[20] however, have shown by electron diffraction experiments that the dimer of formic acid has a ring structure of the form



In either case, since a hydrogen bond is formed between the oxygen atoms of two separate molecules, it seems clear that the bonding between H and O must be different from that in normal OH, with a corresponding effect on the vibration frequency. In fact, Pauling and Brockway showed that the O–O distance in the formic acid dimer is 2.66A, indicating that the O–H distance is perhaps 1.33A, rather than the normal 0.96A.

[14] J. W. Sappenfield, Phys. Rev. **33**, 37 (1929).
[15] O. Eichmann, Zeits. f. Physik **82**, 461 (1933).
[16] A. Roth, Zeits. f. Physik **87**, 192 (1933).
[17] J. Errera and P. Mollet, J. de physique **7**, 281 (1935).
[18] Drucker and Ullman Zeits. f. physik. Chemie **74**, 604 (1910).
[19] Sidgwick, *The Electronic Theory of Valence* (Oxford, 1929).
[20] L. Pauling and L. Brockway, Proc. Nat. Acad. Sci. **20**, 336 (1934).

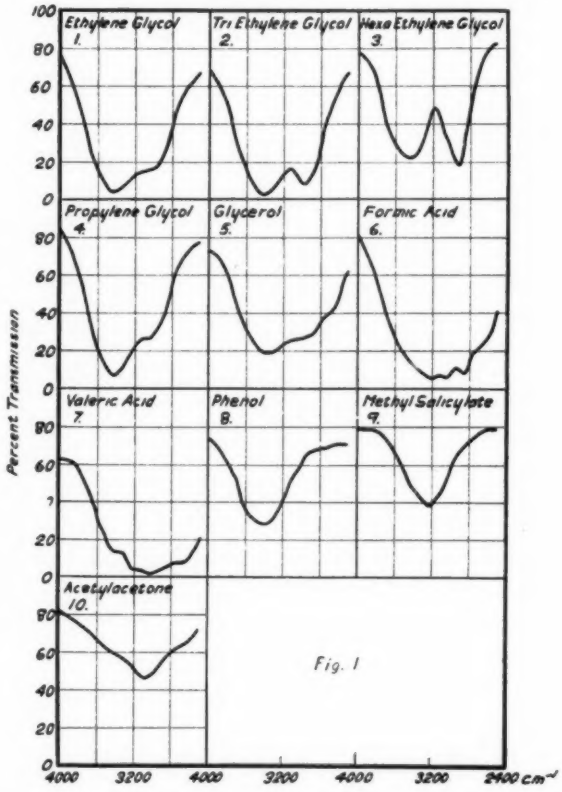


FIG. 1. These infrared transmission curves cover, for several compounds containing the hydroxyl group, the regions of the fundamental OH and CH absorptions at about 3400 and 3000 cm^{-1}, respectively. The absence of the OH absorption is to be noted in formic acid, methyl salicylate and acetylacetone, curves 6, 9 and 10.

Association through linkage of the OH appears to a certain extent in most hydroxyl containing molecules, and the relative intensity of the 3400 absorption region provides an indication as to the extent to which this has taken place. Even the alcohols, which were cited above as showing the OH frequency in the infrared, are known to be slightly associated. Kinsey and Ellis[21] found that the characteristic band, for the case of methyl alcohol, was shifted slightly, sharpened, and increased in intensity by passing from the liquid to a solution in CCl_4. Dilution with a solvent tends, of course, to diminish association, and Kinsey and Ellis found that the absorption in solution bore a close resemblance to that of the vapor, which is almost certainly unassociated. As might be expected, an increase in temperature also has a tendency to decrease the degree of association, as was shown by experiments of Bloch and Errera.[22]

Molecular association is affected by the weight and volume of the interacting molecules, as illustrated by curves 6 and 7. In formic acid the OH absorption is completely lacking, while in valeric there does appear a slight trace of absorption in this region. This same effect has been found by Errera and Mollet,[17] who investigated a series of acids, including caproic, in the overtone region.

Chelated compounds

It has been shown that in a number of compounds, principally aromatic compounds containing an OH in the *ortho* position to a C=O or N=O, the possibility exists of forming a ring. This ring, usually six membered, is closed by a hydrogen bond, again involving the hydrogen of the OH group. Both Sidgwick and Errera and Mollet present much evidence of a chemical and physical nature justifying the ring structure for methyl salicylate, salicylaldehyde and many other similar compounds. The final proof seems to be supplied by the fact that none of these compounds exhibit any OH absorption, as was shown by Errera and Mollet and by Hilbert, Wulf, Hendricks and Liddel[23] by measurements in the overtone region. Curves 8 and 9, taken in this laboratory, show how, in the fundamental region, the strong OH band of phenol is completely wiped out when the C=O is placed in the *ortho* position to it in methyl salicylate. Acetylacetone, which is known from other evidence to exist almost entirely in the enol form, is also capable of forming a chelate ring, as is shown by the absence of the 3400 band in curve 10.

In the case of these compounds, as also for the fatty acids, it is interesting to speculate as to the fate of this OH absorption band. Certainly, even though the frequency is greatly affected, there must still be some vibration characteristic of the motion of H against O, though it has not yet been located. It seems reasonably certain that the strength of such a hydrogen bond is only a small fraction of that of the normal OH bond. That is to say, the dissociation energy of the O−H−O link formed in associated or chelated compounds

[21] E. L. Kinsey and J. W. Ellis, Phys. Rev. **49**, 105 (1936).

[22] B. Bloch and J. Errera, J. de physique **6**, 154 (1935).

[23] Hilbert, Wulf, Hendricks and Liddel, Nature **135**, 147 (1935).

is of the same order of magnitude as that of an ordinary OH. In formic acid Pauling and Brockway found, however, that the distance between two oxygen atoms bound by a hydrogen bond was about 2.67A, which agrees well with previous crystal structure values, and with distances calculated by Errera and Mollet from known angles and distances alone. If, then, the H atom remains at approximately the normal distance of 0.96A from the oxygen to which it was originally bonded it will be 1.71A from the other. It is known that interatomic forces decrease very rapidly with distance so the vibration in this case would be essentially H against one O and the energy consideration given above would indicate that the frequency would be almost unchanged. Since this is obviously not so, let us turn to the perhaps more reasonable case of the hydrogen atom midway between the two oxygens, with the force so distributed that each OH bond is the same. Assuming that the force constant varies with distance in the inverse cube fashion suggested by Badger[24] it is possible to calculate the OH vibration frequency for this case. Assuming further that the oxygen atoms are stationary and that the equilibrium O−H distance is 1.33A we find, that the 3400 cm^{-1} frequency shifts to nearer 2400. However, it is not necessary that the H lie on the O−O line and the O−H separation may be larger than that used above. Below are given frequency values corresponding to several O−H separations, taking the O−O distance constant at 2.67A.

r	1.33	1.40	1.50	1.60	1.70
$\tilde{\nu}$	2390	2050	1680	1390	1170.

In a recent paper Gillette and Sherman[25] seem to favor a structure for the formic acid dimer in which the hydrogen atom, while located on the line of centers of the oxygen atoms, is neither in the center nor at the normal O−H distance from one. This would lead to a vibration frequency between the above 2400 and 3400 cm^{-1}. It would appear from this that almost any value of the OH frequency in compounds of this type would be reasonable, and it is unfortunate that as yet no spectrum has been analyzed carefully enough to permit of its identification.

[24] R. M. Badger, J. Chem. Phys. **2**, 128 (1934).

[25] R. H. Gillette and A. Sherman, J. Am. Chem. Soc. **58**, 1135 (1936).

DECEMBER, 1936 JOURNAL OF CHEMICAL PHYSICS VOLUME 4

The Relative Atomic Weight of Oxygen in Water and in Air

II. A Note on the Relative Atomic Weight of Oxygen in Fresh Water, Salt Water and Atmospheric Water Vapor

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(Received September 12, 1936)

Purified Lake Michigan water appears to be nearly exactly intermediate in density between purified Atlantic Ocean water and water condensed from the atmosphere. Within the experimental error the entire difference in density between fresh and salt water appears to be due to differences in the oxygen isotopic ratios. The bearing of these results on theories explaining the relatively large concentration of O^{18} in the atmosphere is discussed.

IN applying[1] the isotopic exchange theory of Urey and Greiff[2] to the interpretation of the relatively large concentration of O^{18} in the atmosphere, the author estimated that of the difference in density between purified salt water and fresh water amounting to 1.9 p.p.m. approximately 1.6 p.p.m. was due to a difference in the isotopic ratio of oxygen. Greene and Voskuyl[3] state, "yet it is improbable that more than 1 p.p.m. . . . is due to the oxygen isotopes." There is also the possibility that fresh water might have the same isotopic composition as atmospheric water vapor. In order to answer these questions

[1] M. Dole, J. Chem. Phys. **4**, 268 (1936).

[2] H. C. Urey and L. J. Greiff, J. Am. Chem. Soc. **57**, 321 (1935).

[3] C. H. Greene and R. J. Voskuyl, J. Am. Chem. Soc. **58**, 693 (1936).

TABLE I. *Density data for purified Atlantic Ocean water and water condensed from the atmosphere.*

Source of Water	Δt	γ
Atlantic Ocean	+0.006 (P)	+1.5
	+0.005 (Q)	+1.5
Atmosphere		
Sample I	−0.0045 (P)	−1.3
	−0.005 (P)	−1.4
Sample II	−0.007 (Q)	−2.1
	−0.010 (Q)	−3.0
Average of atmosphere water	−0.0066	−1.95

(*P*) signifies measurement made with a Pyrex float at 29.0°; (*Q*) signifies a quartz float used at 29.9°; γ is the difference in density between these waters and normal (purified Lake Michigan) water expressed in parts per million.

it was decided to measure the differences in density between these three sources of water and to determine the roles of the oxygen and hydrogen isotopes in producing these differences.

In the author's application of the Urey and Greiff theory the fractionation factor 1.014 for the separation of the oxygen isotopes when water evaporates from a large body of water was also used, but here again this was only a reasonable estimate since this factor depends upon the temperature[4] and it is not known at what temperature water vapor is in equilibrium with water of the (which?) ocean. If the relative atomic weight of oxygen between atmospheric water vapor and fresh water is known, then it would be unnecessary to apply the fractionation factor 1.014 and the Urey and Greiff theory could be applied directly without introducing this uncertainty.

EXPERIMENTAL

The ocean water was kindly obtained for us by the U. S. Coast Guard 45 miles east of Cape Ann.[5] Laboratory distilled water which originally comes from Lake Michigan served as the fresh water and water vapor was frozen out of the air by passing air obtained outside of the chemical laboratory through a dry-ice acetone trap at the rate of two to three liters a minute. The air was first passed through a water condenser which cooled the air and in which some water would condense on very humid days. The completeness of the removal of the water vapor from the air was tested by allowing the dried air to pass through a weighed phosphorus pentoxide tube for 17 hours. While 17.8 cc of water were frozen out in the dry-ice trap, the phosphorus pentoxide tube gained only 0.027 gram in weight. The freezing out of the water vapor was carried on continuously from April 27 to May 25, the first 300 cc of water condensed (to May 12) was taken as the first sample and the water obtained (330 cc) from May 12 to May 25 constituted the second sample. We have no assurance that the water frozen out represents a true sample from the isotopic point of view of the water contained in the earth's atmosphere, but since the chemical composition of the atmosphere (when dry) is known to be remarkably constant, we can assume that the isotopic composition of the water vapor in the air is also constant.

TABLE II. *Density data for waters made from the oxygen (after electrolysis) of Atlantic Ocean water, Lake Michigan water and water vapor and from tank hydrogen.*

Source of Oxygen in Water	Δt	γ
Lake Michigan I	−0.040	
	−0.042	
	−0.0426	
II	−0.040	
	−0.039	
Average	−0.0407	−12.2
Atlantic Ocean	−0.034	
	−0.0335	
	−0.038	
Average	−0.0352	−10.6
Water vapor	−0.046	
	−0.0455	
	−0.0455	
Average	−0.0457	−13.7

The purification of the water and the density measurement technique have been repeatedly described in previous papers. The results of the density measurements are given in Table I.

In order to separate these density differences into those due to variations in the oxygen isotope ratios and to variations in the D/H ratio, these waters were electrolyzed along with normal water, the oxygen collected, purified and recombined with tank hydrogen according to the method previously described.[6] The two samples of water collected from the atmosphere were mixed before the electrolysis was carried out. Values of γ after electrolysis are given in Table II. All measurements were made using the quartz float.

[4] M. H. Wahl and H. C. Urey, J. Chem. Phys. **3**, 411 (1935).

[5] We are indebted to Edward Page, Esq., for arranging with the Coast Guard to get this water.

[6] M. Dole, J. Am. Chem. Soc. **58**, 580 (1936).

Discussion

From Table I it is seen that purified Atlantic Ocean water is 1.5 p.p.m. heavier than Lake Michigan water. Greene and Voskuyl[7] found a difference of 1.8 p.p.m. between ocean water and Cambridge, Massachusetts tap water and a difference of 0.4 p.p.m. between Lake Michigan water and Cambridge tap water. Subtracting 0.4 from 1.8 we obtain 1.4 p.p.m. for the excess density of Atlantic Ocean water over Lake Michigan water as given by the work of Greene and Voskuyl. This is in excellent agreement with our result of 1.5 p.p.m. A similar calculation using Gilfillan's datum[8] and the figure 0.4 p.p.m. given by Greene and Voskuyl yields 1.9 p.p.m., not in quite such good agreement. The water condensed from the atmosphere is definitely lighter than Lake Michigan water, in fact, just about as much lighter as the ocean water is heavier than Lake Michigan water. We are not certain whether the different results for samples I and II of the water condensed from the atmosphere represent a real variation or are simply experimental errors.

We are particularly interested in the data of Table II which demonstrate that practically all of the density differences of Table I are due to variations in the oxygen isotope ratios. From Table II it is also evident that the oxygen of Lake Michigan is nearly exactly intermediate in isotopic composition between the oxygen of the Atlantic Ocean and oxygen of atmospheric water vapor. From Table II it can also be calculated that the oxygen isotope fractionation factor for the equilibrium between water vapor and the Atlantic Ocean is 1.014, or exactly the value given by Wahl and Urey[4] for 11.2° (52°F). This is a reasonable result.

We should expect part of the differences in density given in Table I to be due to the hydrogen isotopes; perhaps the difference in density between Lake Michigan water and water from the atmosphere which is not accounted for by the oxygen isotope ratio differences, 0.4 p.p.m., is caused by variations in the D/H ratio, but our work does not appear to be accurate enough to settle the question of the hydrogen isotopes in this case.

[7] C. H. Greene and R. J. Voskuyl, J. Am. Chem. Soc. **56**, 1650 (1934).

[8] E. S. Gilfillan, Jr., J. Am. Chem. Soc. **56**, 406 (1934). This water came from the ocean near Bermuda.

We can now proceed to recalculate the difference in density between water made from atmospheric oxygen and the oxygen of Lake Michigan water expected on the basis of the Urey and Greiff theory. At 223°A the enrichment factor for the equilibrium

$$2H_2O^{18}(g)+O_2^{16}\rightleftarrows O_2^{18}+2H_2O^{16}(g)$$

is 1.0338,[1] which is equivalent to 7.5 p.p.m. difference in water density. Subtracting 1.5 p.p.m. the difference in the density of water condensed from the atmosphere and Lake Michigan water due to the oxygen isotopes as given in Table II we obtain 6.0 p.p.m. as the theoretical difference in density between water made of atmospheric oxygen and the oxygen of Lake Michigan water, the hydrogen in the two waters being identical in isotopic composition. This agrees exactly with our measured difference, and lends strength to the application of the[1] Urey and Greiff theory.

Greene and Voskuyl[3] have recently presented an interesting theory to account for our observed value of 6.0 p.p.m. They assume that carbon dioxide of the atmosphere is in equilibrium with the water of the atmosphere at 0°C. This carbon dioxide is then absorbed by plants where it gives up its two oxygen atoms which become uniformly mixed with one atom in the water molecule of the plant which the carbon dioxide unites with. Two atoms of oxygen are then liberated by the plant and should have the average isotopic composition of the oxygen in the carbon dioxide and the water of the plant. They calculate an expected density difference of 6.8 p.p.m. However, if they had assumed the carbon dioxide water equilibrium to be established at 25°C, they would have obtained 5.7 p.p.m. from their calculations instead of 6.8 p.p.m. The chief difficulty with the theory of Greene and Voskuyl aside from ignorance concerning the isotopic composition of the oxygen in carbon dioxide of the atmosphere is that practically nothing is known concerning the photosynthetic reaction in plants. However, their theory is an entirely plausible one and it may be that both the effect calculated by the author and that suggested by Greene and Voskuyl are operative.

Grateful appreciation is expressed to Mr. B. Z. Wiener for experimental assistance.

Kinetics of OH Radicals as Determined by Their Absorption Spectrum

II. The Electric Discharge Through H_2O_2

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(Received October 5, 1936)

In order to study the kinetics of OH radicals in H_2O_2 the concentration of OH as a function of time is measured by the decay of the intensity of the OH absorption bands after interrupting an electric discharge through H_2O_2. For each snapshot a new supply of H_2O_2 is introduced into the absorption tube and partly decomposed into OH+OH by an electric discharge of brief duration. OH radicals disappear in H_2O_2 much more rapidly than in H_2O. This indicates a bimolecular reaction $OH+H_2O_2$. The emission spectrum of OH shows abnormal rotation of OH even more strongly when excited in H_2O_2 than in H_2O, the rotation being determined not by the temperature but by the simultaneous dissociation and excitation producing the OH radicals observed.

I. Problem

In the preceding paper[1] the reaction of OH as produced in the electric discharge through water vapor has been investigated. The concentration of OH as a function of time after interrupting the discharge was traced by the intensity of the absorption spectrum taken in snapshots; the pressure, in particular of added helium was varied. The main result was that OH is largely consumed by triple collisions—probably $H+OH+M \rightarrow H_2O+M$. The interpretation of the experiments, however, was somewhat complicated by the presence of free hydrogen atoms.

There is a chance to observe a still simpler system in H_2O_2 vapor after the interruption of an electric discharge. It was found by Urey, Dawsey and Rice[2] that in a weak discharge through H_2O_2 the spectrum consists almost exclusively of OH bands. They concluded that in the discharge the most probable process is the dissociation of H_2O_2 into OH+OH and that very little atomic H and O are produced. This discharge, therefore, after its interruption affords an observation of the life of OH radicals when they collide largely with H_2O_2 and with much less probability with other OH radicals.

From previous results one might arrive at contradictory predictions regarding the fate of OH in H_2O_2 vapor. Rodebush and Wahl[3] observed so high a concentration of H_2O_2 in the gas pumped out of the discharge through H_2O vapor that one ought to assume as the most probable process the combination $OH+OH+M \rightarrow H_2O_2+M$ and only a small probability that H_2O_2 thus formed is destroyed again by H or OH. On the other hand Urey, Dawsey and Rice found out that H_2O_2 is decomposed so rapidly by a weak discharge that they had to make their spectroscopic investigation with fast flowing vapor. This apparent discrepancy is probably solved by the recent assumption of Campbell and Rodebush[4] and of Geib[5] that in the gas pumped out of the discharge through H_2O vapor the H_2O_2 is not formed in the gas phase but in the freezing process in the liquid-air trap so that it is not exposed to decomposition. This idea is strongly confirmed by the failure, published in the preceding paper, to observe the absorption spectrum H_2O_2 after interrupting the electric discharge through H_2O in spite of an arrangement which had been made sufficiently sensitive to detect 1/100 mm H_2O_2.

II. Experimental

The experimental arrangement was largely the same as that described in previous papers. The concentration of OH was observed by the intensity of its absorption spectrum taken by snapshots in the second order of a 21-foot grating. H_2O_2 was concentrated from the commercial 30 percent solution (Superoxol) by a vacuum distillation at 0°C, the residue analyzing 95 percent

[1] A. A. Frost and O. Oldenberg, J. Chem. Phys. **4**, 642 (1936).
[2] H. C. Urey, L. H. Dawsey and F. O. Rice, J. Am. Chem. Soc. **51**, 1371 (1929).
[3] W. H. Rodebush and M. H. Wahl, J. Chem. Phys. **1**, 696 (1933).
[4] R. W. Campbell and W. H. Rodebush, J. Chem. Phys. **4**, 293 (1936).
[5] K. H. Geib, J. Chem. Phys. **4**, 391 (1936).

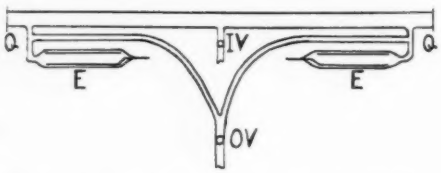

FIG. 1. Discharge and absorption tube for H_2O_2; scale 1: 25; *Q*, quartz window; *E*, electrode; *IV*, inlet valve; *OV*, outlet valve.

H_2O_2 by weight. However, the H_2O_2 vapor derived from this, and used in the following experiments, was only about 50 mole percent H_2O_2 as determined from vapor pressure measurements.

The H_2O_2 vapor had to be kept flowing with considerable velocity through the observation tube since otherwise the products of its decomposition would have accumulated and affected the reaction studied. On the other hand too rapid a flow was not permissible since it would carry away the OH the reaction of which was to be studied after interrupting the discharge.

With this arrangement only very faint absorption spectra of OH were observed. They disappeared entirely after a short time interval. It was questionable, however, whether this failure was caused by inadequate conditions or by the real disappearance of OH. Therefore a fresh supply of H_2O_2 at a definite pressure was introduced for each snapshot of the absorption spectrum. The direction of flow was arranged such that impurities emanating from the electrodes were swept away. The following cycle of operations was carried out automatically with the aid of magnetically operated valves. First the absorption tube was pumped out through short and wide tubes by a very rapid pump (Cenco Hypervac), next the stopcock to the pump closed, H_2O_2 of the proper pressure admitted and partly decomposed by a discharge of about 350 ma (current density 20 ma/cm^2) lasting for 1/120 of a second, and finally the absorption spectrum of OH was taken in a snapshot at a time interval after the discharge that could be varied. This whole process that needed about 4 seconds was repeated 4500 times in order to secure sufficient exposure of the photographic plate.

Because of the long total time required for the exposure it was found convenient to take during the same run two exposures corresponding to two different time intervals between discharge and absorption measurement. This was done by using a rotating sector which allowed light to get into the grating spectrograph through two different portions of the same slit at different times. Since during these experiments the astigmatism of the spectral lines from a concave grating was almost completely removed by a cylindrical lens, the two adjacent portions of the slit formed adjacent portions of the spectral lines.

It is known that H_2O_2 decomposes when in contact with metals or stopcock grease. The aluminum electrodes therefore were kept away from the absorption tube by the arrangement illustrated in Fig. 1. The gas valves only schematically indicated in Fig. 1 were built as shown in Fig. 2. The movable glass core *C* containing a piece of soft iron, sealed in a closely fitting glass tube, rested by its weight on the flange *F* of a glass tube. The flange *F* and the ring forming the bottom of *C* were both ground and polished optically flat, as tested with interference methods.[6] No grease was applied. Only very little gas leaked through this valve when closed. A test showed that the H_2O_2 was not decomposed by flowing through this valve. It must be kept in mind that its purpose was only

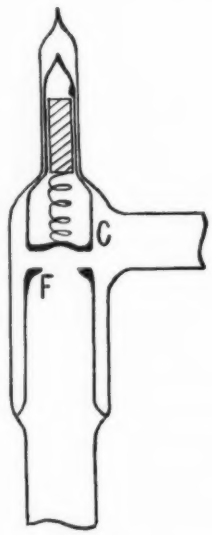

FIG. 2. Greaseless valve, magnetically operated, with optically flat contact; scale 1: 2; *C*, glass core; *F*, flange.

[6] We appreciate the accurate work of Mr. D. W. Mann and Mr. H. W. Leighton who made the valves.

to separate the absorption tube for a few seconds from adjoining tubes which contained pressures different by a few millimeters. When opened by the magnet it offered an outlet much wider than most commercial stopcocks. (This valve must be connected so that when closed the gas pressure acts downward on the core *C*. The strength of the magnet required to open it depends upon the pressure difference.) A synchronous motor with various switches on its axis operated the following five devices: the current through the H_2O_2 vapor (with the aid of a thyratron as a relay), the hydrogen discharge that gave the continuous background for the absorption spectrum, the two magnets for inlet and outlet valve, and finally a sector disk that excluded from the spectrograph the emission spectrum from the flash through the H_2O_2 and admitted only the light for the absorption spectrum.

The absorption spectrum when resolved into rotational lines indicates relative concentrations of OH by a photometric procedure described in the preceding paper.

III. Results

After interrupting the discharge through H_2O_2 the absorption spectrum of OH disappeared at a rate very much higher than in the discharge through H_2O. While in H_2O the absorption of OH could be traced as long as 0.4 sec., in H_2O_2 under similar conditions it was much fainter and disappeared within 1/100 sec. That OH is certainly produced in the discharge is shown by the fact that the OH emission from the discharge through H_2O_2 was even stronger than the OH emission from an H_2O discharge under the same conditions of pressure and current.

Since the main feature of the new experiment consists of the presence of ample H_2O_2, it is most plausible to assume that the rapid disappearance of OH is caused by a bimolecular reaction with H_2O_2. This experiment gives no evidence of the product of this reaction. The rate is too high for accurate measurement with the rotating sector. On the other hand it is certain that only a small fraction of all collisions $OH+H_2O_2$ lead to a reaction.

By observing the continuous absorption spectrum of H_2O_2 it was found that a half-period of rather weak current is sufficient to decompose largely the H_2O_2. This agrees with the statement of Urey, Dawsey and Rice that the emission spectrum of H_2O_2 shows its characteristic feature only if the vapor is rapidly flowing. Since a tendency towards the formation of H_2O is to be assumed, it is plausible that the same process takes place in the vapor $OH+H_2O_2 \rightarrow H_2O+O_2H$ that has been discussed in great detail by Haber and Weiss[7] and by Kornfeld[8] for the decomposition of H_2O_2 in solution.

IV. Abnormal Rotation of OH Caused by Dissociation of H_2O_2

In the electric discharge through water vapor a striking difference has been observed between the intensity distributions in emission and absorption.[9] In absorption only a few rotational quanta appear in each branch corresponding to approximately room temperature. In emission, however, very high rotation is indicated by the long extension of each branch, entirely unrelated to the temperature of the gas; the well-known sharp edge 3064 by which this band is easily identified in emission disappears completely in absorption since its rotational energy value considerably exceeds the thermal value.

The abnormal rotation observed in emission has been explained by the assumption that in the excitation process a fast electron which must have at least 9.0 volts, dissociates the H_2O and excites the OH *in one process*. The energy with which H and OH′ separate is determined not by the temperature but instead by properties of potential curves describing the structure of normal and excited H_2O.[10]

In the electric discharge through H_2O_2, according to Urey, Dawsey and Rice, we similarly assume one process of dissociation and excitation of one of the OH. Since we are dealing with a dissociating molecule of a structure entirely different from H_2O we ought to expect some other value of abnormal rotation although we are unable to predict the value in one or the other case.

[7] F. Haber and J. Weiss, Proc. Roy. Soc. London **A147**, 332 (1934).
[8] G. Kornfeld, Zeits. f. physik. Chemie **B29**, 205 (1935).
[9] O. Oldenberg, Phys. Rev. **46**, 210 (1934).
[10] O. Oldenberg, Phys. Rev. **37**, 1550 (1931).

The experiment described above offers good conditions for such an observation since a brief electric discharge is sent through H_2O_2 vapor and then the partly decomposed vapor is pumped out and replaced by fresh vapor so that the OH band observed is certain to originate from dissociating H_2O_2.

A comparison of the OH bands in H_2O and H_2O_2 actually shows a distinct difference in abnormal rotation. For equal intensities at the low rotational lines in H_2O_2, the tail representing the highest rotation is more intense than in H_2O. This result confirms the idea of the origin of abnormal rotation of OH.

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Solvent Action on Optical Rotatory Power

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A general theory of the optical rotatory power of liquids is developed. The method of C. G. Darwin, supplemented so that the fundamental quantities $s_{\alpha\beta\gamma}\ldots$† which appear there are related to the properties of the molecules comprising the medium, is followed. The optical properties of a molecule are given by a set of tensors $\sigma'_{\alpha\beta\gamma}\ldots$. The concept of deformation leads naturally to a simple relation between the $\sigma'_{\alpha\beta\gamma}\ldots$'s and the field acting on the molecule. The electrostatic field of the dipoles of the surrounding molecules is computed for the limiting cases of imperfect gases and dilute solutions, for molecules of simple geometrical configuration. This field is identified with the solvent field. For these idealized systems, the rotatory power of a molecule in various solvents is determined in terms of quantities characteristic of the solvents. The resulting equations are controlled by comparing with the behavior of actual liquids.

SECTION 1

THE problem of the solvent action on optical rotatory power dates back to within a few years of the discovery of natural gyration itself by Biot.[1] His early work on solutions (1815–1832) led Biot[2] to invent the quantity "specific rotation" which he believed to be characteristic for a particular optically active substance. He concluded from these experiments that each molecule possesses the property of rotating the plane of polarized light a definite amount and that "the active molecules (solute) merely disperse themselves among the inactive molecules (solvent), as if in free space, without suffering from them any action which modifies their rotatory power appreciably."[3] In subsequent experiments however, it was found that all active substances show variations of specific rotation with solvent, concentration and temperature.

The earliest explanation of this solvent action, the tautomerism theory, was closely associated with anomalous rotatory dispersion. Historically, the tautomerism theory arose from studies on tartaric acid. Biot found that tartaric acid solutions not only exhibited a strong solvent effect, but also showed anomalous rotatory dispersion, so-called because the dispersion curve showed a maximum in the visible region. He artificially produced the dispersion anomaly by measuring simultaneously two substances with simple dispersion but opposite rotations.[4] This suggestive idea was explicitly formulated, and applied to the solvent effect, by Arndtsen[5] in 1858. He concluded that anomalous dispersion is caused by the existence of two forms of tartaric acid in solution, varying proportions of the two forms being responsible for the changes of rotation with concentration. The variation of the proportions was later considered to be due to a shift in an equilibrium between the two forms.[6]

Confirmation of the existence of tautomers was obtained from the work on mutarotation in

* Adapted from a dissertation submitted to Columbia University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

† $\sigma_{\alpha\beta\gamma}\cdots$ in Darwin's notation.

[1] J. B. Biot, Mém. acad. sciences **15**, 93 (1838).

[2] J. B. Biot, Mém. acad. sciences **13**, 39 (1835).

[3] J. B. Biot, Ann. chim. phys. (3) **36**, 258 (1852).

[4] J. B. Biot, Comptes rendus **2**, 543 (1836).

[5] A. Arndtsen, Ann. chim. phys. (3) **54**, 403 (1858).

[6] T. M. Lowry and T. W. Dickson, Trans. Faraday Soc. **10**, 96 (1914); T. M. Lowry and P. C. Austin, Phil. Trans. Roy. Soc. **A222**, 249 (1922).

sugars and on enol-keto isomerism, principally late in the 19th century. The theory was further developed by Armstrong and Walker[7] who showed by means of their "characteristic diagrams" that compounds with simple rotatory dispersion could also be interpreted as existing in two tautomeric forms. Latterly, Lucas[8] has generalized the theory by postulating an arbitrary number of tautomers (three for tartaric acid and its esters), and has explained the shift in equilibrium by an interaction between the solvent and each form.

The work of Kuhn,[9] however, has shown that all active compounds must exhibit anomalous rotatory dispersion. The distinction between anomalous rotatory dispersion and simple rotatory dispersion depends, therefore, on a fortuitous choice of spectral regions. The building up of "anomalous" dispersion from two or more "simple" dispersions thus has no physical significance.

While compounds with known tautomers like sugars, enol-keto types, and nitrocamphor adjust their equilibria only over considerable periods of time, following the course of the overwhelming majority of organic reactions, the compounds for which tautomerism is the explanation of the solvent effect show no suspicion of a finite rate of change of rotation. Thus the only proof of the existence of tautomers of these latter compounds is the optical evidence which the tautomers are called upon to explain.

Parallel to the development of the tautomerism theory there arose the somewhat vague concept of deformation to account for the small and not very spectacular changes of rotation of the majority of active compounds. Attempts were made to correlate these changes with internal pressure, changes of molecular size, and so forth; in general, with little success. This idea of deformation was not clearly distinguished from the equally vague ideas of solvation or association.[10, 11]

The above theories, developed when our knowledge of the physical basis of optical rotatory power was small, have failed to give a satisfactory account of the general phenomenon. In view of the criticism[12, 13] to which they are subject, it is clear that we must turn to the modern theories for an explanation of the solvent effect.

With the advent of the electronic theories of optical rotatory power came the realization that the fundamental quantity describing optical activity was not the specific rotation, but a quantity of the form

$$[\alpha]/f(n),$$

where n is the refractive index of the medium.[14–18] The generally accepted value n^2+2 for $f(n)$ found by Gans in his correction of Born's theory, we have confirmed by a more precise derivation from Darwin's general theory.[19] The expression

$$[\alpha]/n^2+2\equiv\Omega$$

bears the same relation to specific rotation as refractivity does to refractive index. We shall, therefore, call it the "rotivity." Experimental attempts have been made to establish the invariance of this quantity, without much success. The experiments of Wolf and Volkmann[20] indicated the reason for this. They found that the law, Ω=constant, was obeyed by systems without dipoles but not by those with dipoles.

The concept of deformation has recently been reestablished on a firm theoretical foundation by de Mallemann[16] and Kuhn.[9] They demonstrated that a minute variation in the position of the virtual oscillators will produce a very large change in rotatory power. This viewpoint, together with an exact specification of the external influence producing the displacement, in terms of the electric moments of the solvent molecules, forms the basis of the theory of solvent action developed in this paper. With the aid of these

[7] H. E. Armstrong and E. E. Walker, Proc. Roy. Soc. **A88**, 388 (1913).
[8] R. Lucas, Trans. Faraday Soc. **30**, 418 (1930).
[9] W. Kuhn, Zeits. f. physik. Chemie **B4**, 14 (1929); W. Kuhn and E. Braun, ibid. **B8**, 281 (1930); W. Kuhn and K. Freudenberg, *Hand- und Jahrbuch der chemischen Physik*, 8, part 3 (Akadem. Verlagsges. M. B. H., Leipzig, 1932).
[10] C. Winther, Zeits f. physik. Chemie **60**, 590 (1907).
[11] T. S. Patterson, J. Chem. Soc. **103**, 145 (1913).
[12] G. Bruhat, Trans. Faraday Soc. **30**, 410, 428 (1930).
[13] T. S. Patterson, Nature **136**, 454 (1935).
[14] M. Born, Physik. Zeits. **16**, 251 (1915); Ann. d. Physik (4) **55**, 177 (1917).
[15] R. Gans, Zeits. f. Physik **27**, 164 (1924); Ann. d. Physik (4) **79**, 547 (1926).
[16] R. de Mallemann, Ann. d. physique (10) **2**, 170 (1924).
[17] G. H. Livens, Phil. Mag. **25**, 817 (1913).
[18] S. F. Boys, Proc. Roy. Soc. **A144**, 655 (1934).
[19] C. G. Darwin, Trans. Camb. Phil. Soc. **23**[6], 137 (1924).
[20] K. L. Wolf and H. Volkmann, Zeits. f. physik. Chemie **B3**, 139 (1929); H. Volkmann, ibid. **B10**, 161 (1930).

two simple concepts, we will find it possible to give a unified quantitative explanation of all the phenomena, as well as empirical formulae, that constitute the solvent effect.

Section 2

The analysis of C. G. Darwin[19] refers the optical properties of a continuous medium to a set of constants $s_{\alpha\beta}$, $s_{\alpha\beta\gamma}$, $\cdots$, which are the coefficients of the expansion of the Hertzian vector Π_α of a material element dV in terms of derivatives of R

$$\Pi_\alpha=\frac{E_\beta dV}{4\pi}\left\{s_{\alpha\beta}+\frac{1}{k}s_{\alpha\beta\gamma}\frac{\partial}{\partial x_\gamma}+\cdots\right\}R, \qquad (1)$$

where $E_\beta e^{ikct}$ is the radiation field due to everything but a small sphere about dV, and

$$R=e^{ik(ct-r)}/r.$$

(The $s_{\alpha\beta}\ldots$ [and the $\sigma_{\alpha\beta}\ldots$] are tensors. The subscripts refer to the tensor components and have the values 1, 2 or 3. The summation convention is used throughout.)

We will refer the $s_{\alpha\beta}\ldots$ to quantities characteristic of the molecules comprising the medium; that is, perform the transition from the actual assemblage of molecules to the ideal continuous medium.

Let $\Delta\tau$ be a small volume element of a fluid, containing N_j molecules of type $j(j=1, 2, \cdots n)$. If $E_\beta{}^m e^{ikct}$ be the actual radiation field on the mth molecule, it will set up a wavelet specified by

$$p_\alpha{}^m=\frac{E_\beta{}^m}{4\pi}\left\{\sigma_{\alpha\beta}{}^m+\frac{1}{k}\sigma_{\alpha\beta\gamma}{}^m\frac{\partial}{\partial x_\gamma}+\cdots\right\}R^m, \qquad (2)$$

where $R^m\equiv\dfrac{e^{ik(ct-r^m)}}{r^m}-;$

$$r^m=[(x_\alpha{}^m-x_\alpha)^2]^{\frac{1}{2}}=[\{(x_\alpha{}^0-x_\alpha)+\Delta^m x_\alpha{}^0\}^2]^{\frac{1}{2}}.$$

The effect at x_α of the entire element is given by the Hertzian vector

$$\Pi_\alpha=\sum_{j=1}^{n}\Pi_\alpha{}^j \qquad (3)$$

where $\Pi_\alpha{}^j$, the contribution to Π_α from molecules of type j, is

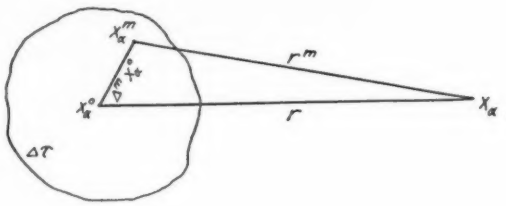


Fig. 1.

$$\Pi_\alpha{}^j=\sum_{m=1}^{N_j}p_\alpha{}^m=\sum_{m=1}^{N_j}\frac{E_\beta{}^m}{4\pi}\left\{\sigma_{\alpha\beta}{}^m+\frac{1}{k}\sigma_{\alpha\beta\gamma}{}^m\frac{\partial}{\partial x_\gamma}+\cdots\right\}R^m. \qquad (4)$$

Now

$$f(r^m)=f(r)+\Delta^m x_\alpha{}^0\frac{\partial}{\partial x_\alpha{}^0}f(r)+\Delta^m x_\alpha{}^0\Delta^m x_\beta{}^0\cdot\frac{1}{2!}\frac{\partial^2}{\partial x_\alpha{}^0\partial x_\beta{}^0}f(r)+\cdots$$

$$=f(r)-\Delta^m x_\alpha{}^0\frac{\partial}{\partial x_\alpha}f(r)+\Delta^m x_\alpha{}^0\Delta^m x_\beta{}^0\cdot\frac{1}{2!}\frac{\partial^2}{\partial x_\alpha\partial x_\beta}f(r)-\cdots,$$

whenever $f(\rho)$ is analytic for $|\rho|\leqq|r^m-r|$. (ρ complex.)

Hence, for x_α outside of $\Delta\tau$

$$R^m=R-\Delta^m x_\gamma{}^0\frac{\partial}{\partial x_\gamma}R+\frac{\Delta^m x_\gamma{}^0\Delta x_\delta{}^0}{2!}\cdot\frac{\partial^2}{\partial x_\gamma\partial x_\delta}R-\cdots \qquad (5)$$

and $E_\beta{}^m e^{ikct}=A_\beta e^{ik(ct-\mu_\alpha x_\alpha{}^m)}$

$$=\{1+(x_\alpha{}^m-x_\alpha{}^0)(-ik\mu_\alpha)+\cdots\}E_\beta{}^0 e^{ikct}. \qquad (5')$$

From (4), (5) and (5′)

$$\Pi_\alpha{}^j=\frac{E_\beta{}^0+\Delta^m x_\alpha{}^0(-ik\mu_\alpha)E_\beta{}^0+\cdots}{4\pi}$$

$$\times\left\{\sum_{m=1}^{N_j}\sigma_{\alpha\beta}{}^m+\left[\frac{1}{k}\sigma_{\alpha\beta\gamma}{}^m-\Delta^m x_\gamma{}^0\sigma_{\alpha\beta}{}^m\right]\frac{\partial}{\partial x_\gamma}+\left[\frac{1}{k^2}\sigma^m{}_{\alpha\beta\gamma\delta}-\Delta^m x_\delta{}^0\cdot\frac{1}{k}\sigma_{\alpha\beta\gamma}{}^m+\frac{\Delta^m x_\gamma\Delta^m x_\delta{}^0}{2!}\sigma_{\alpha\beta}{}^m\right]\frac{\partial^2}{\partial x_\gamma\partial x_\delta}+\cdots\right\}R.$$

Let $\sigma'_{\alpha\beta\gamma}\ldots$ be the tensors $\sigma_{\alpha\beta\gamma}\ldots$ referred to a set of axes (x_1', x_2', x_3') fixed in the molecule. The equations relating the two sets of axes are:

$$x_\beta'=l_{\alpha\beta}x_\alpha, \quad x_\alpha=l_{\alpha\beta}x_\beta'.$$

Then

$$\sigma^{m}{}_{\alpha\beta\gamma\delta\cdots}=l_{\alpha\xi}{}^{m}l_{\beta\eta}{}^{m}l_{\gamma\zeta}{}^{m}l_{\delta\theta}{}^{m}\cdots\sigma'_{\xi\eta\zeta\theta\cdots}, \quad (6)$$

where $\sigma'_{\xi\eta\zeta\theta\cdots}$ (j) is the same for each of the N_j molecules of type j.

Neglecting interaction

Let (x_1', x_2', x_3') be given with respect to the fixed axes (x_1, x_2, x_3) by the usual Eulerian coordinates. Under the specification that the $\Delta\tau$'s in the medium are precisely alike (this neglects the light scattering which is responsible for the blue of the sky), we set $N_j=n_j\Delta\tau$ where $n_j=$number of j type molecules per cc. Performing the transition from an actual fluid to a continuous medium,

$$\Delta\tau\to dV, \quad \Delta^{m}x_{\alpha}{}^{0}\to 0$$

$$\sum_{m=1}^{N_j}\sigma_{\alpha\beta}{}^{m}=\sum_{m=1}^{N_j}l_{\alpha\xi}{}^{m}l_{\beta\eta}{}^{m}\sigma'_{\xi\eta}\to\frac{n_j dV}{8\pi^2}\times\int_0^{2\pi}d\varphi\int_0^{2\pi}d\psi\int_0^{\pi}l_{\alpha\xi}l_{\beta\eta}\sin\theta d\theta, \quad (7)$$

$$\sum_{m=1}^{N_j}\sigma_{\alpha\beta\gamma}{}^{m}=\sum_{m=1}^{N_j}l_{\alpha\xi}{}^{m}l_{\beta\eta}{}^{m}l_{\gamma\zeta}{}^{m}\sigma'_{\xi\eta\zeta}\to\frac{n_j dV}{8\pi^2}\sigma'_{\xi\eta\zeta}\times\int_0^{2\pi}d\varphi\int_0^{2\pi}d\psi\int_0^{\pi}l_{\alpha\xi}l_{\beta\eta}l_{\gamma\zeta}\sin\theta d\theta. \quad (8)$$

The integrations in (7) and (8) are straightforward. We find as a result

$$\sum_{m=1}^{N_j}\sigma_{\alpha\beta}{}^{m}\to\frac{n_j dV}{3}\sigma'_{\xi\eta}(\xi\eta)(\alpha\beta) \quad (\alpha\beta)=\begin{cases}0 & \alpha\neq\beta\\ 1 & \alpha=\beta\end{cases} \quad (9)$$

$$\sum_{m=1}^{N_j}\sigma_{\alpha\beta\gamma}{}^{m}\to\frac{n_j dV}{6}\sigma'_{\xi\eta\zeta}[\xi\eta\zeta][\alpha\beta\gamma], \quad (10)$$

where $[\xi\eta\zeta]=0$ for all values except

$$[123]=[231]=[312]=-[213]=-[132]=-[321]=+1.$$

The duplicate rule[21]

$$\sigma'_{\alpha\beta\gamma\delta\epsilon\cdots}(\theta\zeta)=0$$

if $(\theta\zeta)$ is $(\beta\gamma)$, $(\beta\delta)$, $(\beta\epsilon)\cdots$, $(\gamma\delta)$, $(\gamma\epsilon)\cdots$, $(\delta\epsilon)\cdots$, $\cdots$, applied to $\Pi_{\alpha}{}^{j}$, vanishes the remaining coefficients.

[21] Darwin, reference 19, p. 150.

Putting (9) and (10) into the expression for $\Pi_{\alpha}{}^{j}$ yields

$$\Pi_{\alpha}{}^{j}=\frac{E_{\beta}{}^{0}}{4\pi}\left\{\frac{n_j dV}{3}\sigma'_{\xi\eta}(\xi\eta)(\alpha\beta)+\frac{1}{k}\frac{n_j dV}{6}\sigma'_{\xi\eta\zeta}[\xi\eta\zeta][\alpha\beta\gamma]\frac{\partial}{\partial x_{\gamma}}\right\}R. \quad (11)$$

Comparing this with the form (1), and identifying $E_{\beta}{}^{0}$ with E_{β},

$$s_{\alpha\beta}=\sum_{j=1}^{n}\frac{n_j}{3}\sigma'_{\xi\eta}(\xi\eta)(\alpha\beta) \quad (12)$$

$$s_{\alpha\beta\gamma\delta}=0 \quad \cdots \quad \cdots$$

$$s_{\alpha\beta\gamma}=\sum_{j=1}^{n}\frac{n_j}{6}\sigma'_{\xi\eta\zeta}[\xi\eta\zeta][\alpha\beta\gamma]. \quad (13)$$

It is shown by Darwin that if $s_{\alpha\beta}$ is of the form $s_0(\alpha\beta)$ and $s_{\alpha\beta\gamma}$ of the form $s_1[\alpha\beta\gamma]$, then[22]

$$3\cdot\frac{n^2-1}{n^2+2}=s_0, \quad (14)$$

$$\alpha=\frac{\pi}{\lambda_{\text{vac.}}}\cdot\frac{n^2+2}{3}\cdot s_1, \quad \alpha=\text{rotation/cm}. \quad (15)$$

From (13) and (15) we can obtain the fundamental relationships between stereochemistry and optical rotatory power. The rotatory power of a molecule vanishes if and only if

$$\sigma_1'\equiv\sigma'_{\xi\eta\zeta}[\xi\eta\zeta]=0. \quad (16)$$

Let G be the group of symmetry operations belonging to the molecule. Each operation in G may be specified by a change of axes. Under an arbitrary change of axes

$$\sigma''_{\alpha\beta\gamma\cdots}=l_{\alpha\xi}l_{\beta\eta}l_{\gamma\zeta}\cdots\sigma'_{\xi\eta\zeta\cdots} \quad (17)$$

and under G

$$\sigma''_{\alpha\beta\gamma\cdots}=\sigma'_{\alpha\beta\gamma\cdots}. \quad (18)$$

Let T be the operation of reflection.

$$T: \quad l_{11}=-1 \quad l_{22}=l_{33}=+1.$$

Denoting the molecule obtained by T by a double prime,

$$\sigma_{123}''=l_{1\xi}l_{2\eta}l_{3\zeta}\sigma_{\xi\eta\zeta}'=-\sigma_{123}' \text{ etc.}$$

hence

$$\sigma_1''=-\sigma_1'.$$

Therefore, *two molecules which are mirror images have equal and opposite rotations.*[23] If T belongs to G, $\sigma_1''=\sigma_1'=0$. Therefore, *a necessary condition that a molecule exhibit natural gyration is that it be nonsuperposable with its mirror image.*[24]

[22] Eq. (15), although not written explicitly, follows immediately from (22.2), Darwin, reference 19, p. 162.

[23] L. Pasteur, Comptes rendus **35**, 176 (1852).

[24] L. Pasteur, Alembic Club Reprints **14**, 24.

Similarly, we can show that association is without effect on rotatory power.[25]

The fundamental Eq. (6) is true only when the effect on the mth molecule of the electrostatic fields of all the other molecules of the medium, $\mathbf{F}^m$, is neglected. Dropping this restriction, we have, in general

$$\sigma_{\alpha\beta\gamma}{}^m\ldots = l_{\alpha\xi}{}^m l_{\beta\eta}{}^m l_{\gamma\zeta}{}^m \cdots \sigma'_{\xi\eta\zeta}\ldots(\mathbf{F}^m). \quad (19)$$

Eq. (8) is then replaced by

$$\sum_{m=1}^{N_j} \sigma_{\alpha\beta\gamma}{}^m \rightarrow \frac{n_j dV}{8\pi^2}[\sigma'_{\xi\eta\zeta}(\mathbf{F})]_{\mathrm{av}} \int_0^{2\pi} d\varphi \int_0^{2\pi} d\psi \int_0^{\pi} \times l_{\alpha\xi} l_{\beta\eta} l_{\gamma\zeta} \sin\theta d\theta, \quad (20)$$

where the average is taken over all positions and orientations of all the molecules of the fluid relative to the mth molecule. From (10) and (13)

$$s_{\alpha\beta\gamma} = \sum_{j=1}^{n} \frac{n_j}{6}[\sigma'_{\xi\eta\zeta}(\mathbf{F})]_{\mathrm{av}}[\xi\eta\zeta][\alpha\beta\gamma]$$

and from (15)

$$\alpha = \frac{\pi}{\lambda_{\mathrm{vac.}}} \frac{n^2+2}{3} \sum_{j=1}^{n} \frac{n_j}{6}[\sigma'_{\xi\eta\zeta}(\mathbf{F})]_{\mathrm{av}}[\xi\eta\zeta]. \quad (21)$$

Section 3

We know that $\sigma'_{\xi\eta}$, the scattering coefficient which determines the refractivity, varies in a uniform electric or magnetic field according to the law

$$\sigma'_{\xi\eta}(\mathbf{F}) = \sigma'_{\xi\eta}(0) + \sigma'_{\xi\eta}{}^{\delta}F_\delta + \sigma'_{\xi\eta}{}^{\delta\gamma}F_\delta F_\gamma,$$

the small coefficients $\sigma'_{\xi\eta}{}^{\delta}$ and $\sigma'_{\xi\eta}{}^{\delta\gamma}$ contributing to the Faraday effect, the Cotton-Mouton effect, the Kerr effect, and so forth.[26] However, the fact that the refractivities are additive in solvent pairs such as heptane-ethyl iodide, $CCl_4 - CH_3COCH_3$, $CCl_4 - CH_3COOCH_3$, and ethyl bromide-ethanol to 0.07 percent,[27] indicates that the sources of variation of refractivity are unable to account for the variations of the rotivity of the observable magnitude. The essential feature by which $\sigma'_{\xi\eta\theta}[\xi\eta\theta]$ differs from $\sigma'_{\xi\eta}(\xi\eta)$ is the explicit dependence of the former on the positions of the atoms: $\sigma'_{\xi\eta}(\xi\eta)$ is completely independent of the positions of the atoms, the refractivities of organic compounds being an additive function of the refractivity of the constituent atoms.[28]

We conclude that the variations of $\sigma'_{\xi\eta\theta}[\xi\eta\theta]$ in solvent fields should be attributed to the changes in position of the atoms. This is precisely the concept of deformation.[16]

Accordingly we set

$$\sigma'_{\xi\eta\zeta}(\mathbf{F}) = \sigma'_{\xi\eta\zeta}(\mathbf{q}^1, \mathbf{q}^2, \cdots \mathbf{q}^t) \equiv \sigma'_{\xi\eta\zeta}(\mathbf{q}^k),$$

where $\mathbf{q}^k$ is the position vector of the kth atom with respect to an arbitrary origin in the molecule, and

$$\mathbf{q}^k = \mathbf{q}_0{}^k + \mathbf{u}^k(\mathbf{F})$$

$\mathbf{u}^k(\mathbf{F})$ being the displacement of the kth atom from rest under influence of the uniform external field $\mathbf{F}$. Then

$$\sigma'_{\xi\eta\zeta}(\mathbf{q}^k) = \sigma'_{\xi\eta\zeta}(\mathbf{q}_0{}^k) + \frac{\partial\sigma'_{\xi\eta\zeta}(\mathbf{q}_0{}^k)}{\partial q_{0\alpha}{}^s} u_\alpha{}^s + \cdots,$$

discarding higher terms on the assumption that $\mathbf{u}$ is small. We assume that $u_\alpha{}^s = \varphi_{\alpha\delta}{}^s F_\delta$, where $\varphi_{\alpha\delta}{}^s$ is the deformability tensor for the sth particle. Then

$$\sigma'_{\xi\eta\zeta}(\mathbf{q}^k) = \sigma'_{\xi\eta\zeta}(\mathbf{q}_0{}^k) + \left\{\frac{\partial\sigma'_{\xi\eta\zeta}(\mathbf{q}_0{}^k)}{\partial q_{0\alpha}{}^s}\varphi_{\alpha\delta}{}^s\right\} F_\delta$$

or, returning to the F notation

$$\sigma'_{\xi\eta\zeta}(\mathbf{F}) = \sigma'_{\xi\eta\zeta}(0) + \sigma'_{\xi\eta\zeta}{}^{\delta}F_\delta \quad (22)$$

with

$$\sigma'_{\xi\eta\zeta}{}^{\delta} \equiv \frac{\partial\sigma'_{\xi\eta\zeta}(\mathbf{q}_0{}^k)}{\partial q_{0\alpha}{}^s}\varphi_{\alpha\delta}{}^s. \quad (23)$$

[25] Suppose that two molecules, 1 and 2, are associated and move in unison. The contribution to $6s_{\alpha\beta\gamma}$ by these molecules is

$$\{\sigma'_{1\xi\eta\zeta} + \sigma''_{2\xi\eta\zeta}\}[\xi\eta\zeta],$$

choosing as axes for the whole system the axes of molecule 1: $\sigma''_{2\xi\eta\zeta}$ is now the scattering tensor of the 3rd rank of molecule 2 referred to the axes of 1. But, if $l_{\alpha\beta}$ be the direction-cosines of the transformation from the axes of 1 to the axes of 2,

$$\sigma''_{2\xi\eta\zeta}[\xi\eta\zeta] = l_{\xi\alpha}l_{\eta\beta}l_{\zeta\gamma}\sigma'_{2\alpha\beta\gamma}\cdot l_{\xi\theta}l_{\eta\varphi}l_{\zeta\psi}[\theta\varphi\psi] = \sigma'_{2\alpha\beta\gamma}(\alpha\theta)(\beta\varphi)(\gamma\psi)[\theta\varphi\psi] = \sigma'_{2\alpha\beta\gamma}[\alpha\beta\gamma].$$

The contribution to $6s_{\alpha\beta\gamma}$ of the associated pair is then

$$\sigma'_{1\xi\eta\zeta}[\xi\eta\zeta] + \sigma'_{2\xi\eta\zeta}[\xi\eta\zeta],$$

which is precisely the same as that of an unassociated pair. We conclude that association without interaction is without effect on rotatory power, and that a compound built up from optically active compounds without rearrangement or distortion will exhibit optical superposition.

[26] M. Born *Optik* (Springer, Berlin, 1933), p. 346, Eq. (4), also Sec. 78, 79, 80.

[27] C. P. Smyth, E. W. Engel and E. B. Wilson, J. Am. Chem. Soc. **51**, 1736 (1929).

[28] F. Eisenlohr, *Spektrochemie Organische Verbindungen* (F. Enke, Stuttgart, 1912).

If the field is nonuniform, the F_δ must be interpreted as the field at some fiducial point in the molecule, and other terms in $\partial F_\delta/\partial x_\beta$, $\partial^2 F_\delta/\partial x_\beta \partial x_\gamma$, and so forth, must be added to the right of (22). We take no further notice of these terms since they will be shown to contribute nothing to $[\sigma_{\xi\eta\theta}'(\mathbf{F})]_{\text{av}}$.

We note that the above considerations are consistent with the work of Kuhn,[29] who relates solvent changes of rotation with changes in the anisotropy of the circularly dichroic absorption bands. The latter, according to Kuhn's theory[30] are directly connected with changes in the atomic distances and angles.

For a system containing only one optically active substance we obtain from (21) and (22) an expression for the rotatory power, namely,

$$\alpha=\frac{\pi}{\lambda_{\text{vac.}}}\cdot\frac{n^2+2}{3}\cdot\frac{n_j}{6}\{\sigma'_{\xi\eta\zeta}(0)+\sigma'_{\xi\eta\zeta^\delta}(F_\delta)_{\text{av}}\}[\xi\eta\zeta]. \tag{24}$$

Since $(F_\delta)_{\text{av}}$ is (Section 4) of the order 10^3 e.s.u., $\sigma'_{\xi\eta\theta^\delta}$ need be only 0.01 percent of $\sigma'_{\xi\eta\theta}(0)$ for a 10 percent change in rotatory power. The second term in $\{\}$ is responsible for the change of rotation with solvent. $\sigma'_{\xi\eta\theta^\delta}$ *need not* be of the same sign as $\sigma'_{\xi\eta\theta}(0)$. If $\sigma'_{\xi\eta\theta}(0)$ should be small, and $\sigma'_{\xi\eta\theta^\delta}$ of the opposite sign, for some values of $(F_\delta)_{\text{av}}$ the rotation will be positive, for others, negative.

According to Kuhn's theory[9, 30], for example, the actual expression for $\sigma'_{\xi\eta\theta}(0)[\xi\eta\theta]$ is of the form $\sum_i(A_i/(\lambda_i^2-\lambda^2))$, where A_i depends on the intramolecular distances and angles. Thus $\sigma'_{\xi\eta\theta^\delta}[\xi\eta\theta]$ is of the form $\sum_i(B_i/(\lambda_i^2-\lambda^2))$. In spectral regions where one Drude term suffices, the dispersion of $\sigma'_{\xi\eta\zeta^\delta}[\xi\eta\zeta]$ is the same as the dispersion of $\sigma'_{\xi\eta\zeta}(0)[\xi\eta\zeta]$; if more than one Drude term is required, the dispersions will be different.

Eq. (24) shows that the rotivity is the sum of the contributions of two terms whose relative magnitude is variable. Therefore, optically active substances behave *as if* there are two substances (in general, with different dispersions) present in solution. Consequently, the graphical analyses[31] and correlations of data based on the assumption of tautomers can equally well be accounted for by the concept of deformation. The fact that the variations in rotatory power with temperature fall on the same "characteristic diagram" as those caused by solvents,[32] indicates that the temperature effect is only an indirect solvent effect. (See Section 7, part I.D.)

It has also been noticed that a series of related compounds have the same "characteristic diagram."[33] This effect can by no means be explained in terms of tautomers. If we let $\sigma'_{\xi\eta\theta}[\xi\eta\theta]\times$constant represent the contribution to the rotivity of a single circularly-dichroic absorption band common to all the compounds, then this can be split up into

$$\text{constant}\times\{\sigma'_{\xi\eta\zeta}(0)+\sigma'_{\xi\eta\zeta^\delta}(F_\delta)_{\text{av}}\}[\xi\eta\zeta]$$

as before, with $(F_\delta)_{\text{av}}$ now representing the average field of the rest of the molecule. The "vicinal action" of the substituent groups, therefore, in no wise differs, except possibly in magnitude, from the solvent action. If the substituent group is polar and free to rotate, $(F_\delta)_{\text{av}}\sim\mu^2/3kT$ (Section 6). Such an experimental relationship between $[\alpha]$ and the polarity of the substituent group has already been found by Betti.[34]

Section 4

Eq. (24) shows that the change of rotivity depends on the vector value of F.[35] Only those fields whose average components on the $(x_1'x_2'x_3')$ set of axes do not vanish will contribute to the change of rotivity. If the motion of a molecule with respect to the $(x_1'x_2'x_3')$ set of axes is random, the field of the solvent molecule will have no effect no matter what the field may be. Therefore, the whole of the solvent fields measured by the change in rotivity will be the result of deviations from random distribution (with respect to the solute molecules) of the solvent molecules caused by the solute molecules.

With this in mind, we consider the limiting case where the solvent is a continuous medium.[36] We suppose the molecule to occupy a spherical cavity C (of radius a) in a continuous infinite medium of dielectric constant ϵ. Let $V(r, \theta, \psi)$ be the potential function of the molecule. As a

[29] W. Kuhn, K. Freudenberg and R. Seidler, Zeits. f. physik. Chemie **B13**, 379 (1931).

[30] W. Kuhn and K. Bein, Zeits. f. physik. Chemie **B22**, 406 (1933).

[31] T. M. Lowry, *Optical Rotatory Power* (Longmans, Green & Co., London, 1935), Chap. 32.

[32] T. S. Patterson, J. Chem. Soc. **109**, 1176 (1916).

[33] R. H. Pickard and J. Kenyon, J. Chem. Soc. **105**, 844, 1118, 2269 (1914).

[34] M. Betti, Trans. Faraday Soc. **30**, 337 (1930).

[35] Therefore, the work of Holtsmark [J. Holtsmark, Ann. d. Physik (4) **58**, 577 (1919); Physik. Zeits. **25**, 79 (1924)], who computed the probability function for the scalar values of F to account for the broadening of spectral lines by foreign gases, does not apply.

[36] F. C. Frank, Proc. Roy. Soc. **A152**, 171 (1935); K. Higasi, Sci. Papers Inst. Phys. Chem. Research **28**, 284 (1936).

result of the field of the molecule, a distribution of charge is induced on the walls of the cavity; the field of this charge distribution is the solvent field. Let U be the potential of the dielectric. Let U_i be the function U inside C, U_0 the function U outside C. Supposing V unaltered by the fields of dielectric, U satisfies the following schedule of conditions:[37]

$$\nabla^2 U=0, \quad [U_0]_{r=a}=[U_i]_{r=a},$$
$$\epsilon\left[\frac{\partial U_0}{\partial r}\right]_{r=a}-\left[\frac{\partial U_i}{\partial r}\right]_{r=a}=(1-\epsilon)\left[\frac{\partial V}{\partial r}\right]_{r=a}, \tag{25}$$
$$[U_i]_{r=0}=\text{finite}; \quad [U_0]_{r=\infty}=0.$$

Let V be the potential of a permanent electric dipole $\boldsymbol{\mu}$ at 0.

$$V=\frac{\boldsymbol{\mu}\cdot\mathbf{r}}{r^3}=\frac{\mu\cos\theta}{r^2}, \tag{26}$$

$$U_i=-\frac{2\mu}{a^3}\left(\frac{\epsilon-1}{2\epsilon+1}\right)\cdot r\cos\theta=-\frac{2\mu z}{a^3}\left(\frac{\epsilon-1}{2\epsilon+1}\right),$$
$$U_0=-2\mu\left(\frac{\epsilon-1}{2\epsilon+1}\right)\frac{\cos\theta}{r^2} \tag{27}$$

satisfy (25) and represent the potential of the dielectric. The solvent fields are

$$F_x=-\frac{\partial}{\partial x}U_i=0, \quad F_y=-\frac{\partial}{\partial y}U_i=0,$$
$$F_z=-\frac{\partial}{\partial z}U_i=\frac{2\mu}{a^3}\left(\frac{\epsilon-1}{2\epsilon+1}\right). \tag{28}$$

This equation agrees with the two experimental facts:

(i) The rotivity is constant for solutes with no dipole moment but varies widely for solutes with dipole moments.[20]

(ii) The change in rotivity of a given compound in various solvents is a function of the dielectric constant of the solvent,[38] or, otherwise stated, depends on the polarity of the solvent.[39]

Two points are important in the above formulae: first, $\mathbf{F}$ is uniform over the entire molecule, and second, $\mathbf{F}$ is additive as far as the dipole of the active molecule is concerned. The former justifies the dropping of the gradient terms in (22); in what is to follow we will assume the field to be uniform over the molecule, and will only evaluate it at the center of the molecule. (Compare Holtsmark[35].)

This treatment, although helpful intuitively, is subject to serious objections. A solvent is not a continuous medium. The dielectric constant defines the electrical properties of a medium only for gross quantities and large dimensions: it cannot take account of the fact that a substance like *p*-dinitro benzene, for example, acts like a strongly polar substance, although its moment is zero. We therefore turn to a statistical treatment.

Section 5

For simplicity we consider only the case of a 3-component system: composed of an active compound and two inactive compounds. The partition function for the potential energy of the assembly is[40, 41]

$$B(\vartheta)=\int\cdots\int_{\substack{\text{all accessible}\\ \text{phase space}}}\vartheta^W\Pi_k(d\omega)^{N_k},$$

$$\Pi_k(d\omega)^{N_k}\equiv\prod_{r=1}^{N_\alpha}d\omega_{\alpha r}\prod_{s=1}^{N_\beta}d\omega_{\beta s}\prod_{t=1}^{N_\gamma}d\omega_{\gamma t}$$

$$d\omega_{\alpha r}=(dx_\alpha dy_\alpha dz_\alpha\sin\theta_\alpha d\theta_\alpha d\varphi_\alpha d\psi_\alpha)_r$$
$$\cdots\cdots\cdots\cdots\cdots$$
$$\cdots\cdots\cdots\cdots\cdots$$

where x_α, y_α, z_α are the Cartesian coordinates and θ_α, φ_α, ψ_α the Eulerian coordinates of an α-molecule referred to some arbitrary system of axes. There are similar expressions for $d\omega_{\beta s}$ and $d\omega_{\gamma t}$. $\vartheta=\exp(-1/kT)$ and W is the potential energy of the whole assembly. The electrostatic field of all the other molecules acting on a given α-molecule is

$$F_\delta=\sum_{r=2}^{N_\alpha}F_{(\alpha r)_\delta}+\sum_{s=1}^{N_\beta}F_{(\beta s)_\delta}+\sum_{t=1}^{N_\gamma}F_{(\gamma t)_\delta}, \tag{29}$$

where $F_{(\beta s)_\delta}$ is the δ-component ($\delta=1, 2, 3$) (corresponding to three Cartesian axes in the chosen α-molecule) of the field of the sth β-molecule at the chosen α-molecule. The average field is given by

$$[F_\delta]_{av}=\int\cdots\int F_\delta\vartheta^W\Pi_k'(d\omega)^{N_k}/B'(\vartheta), \tag{30}$$

where $$\Pi_k'(d\omega)^{N_k}d\omega_{\alpha 1}=\Pi_k(d\omega)^{N_k}$$

and $$\int d\omega_{\alpha 1}B'(\vartheta)=B(\vartheta).$$

We have

$$[F_\delta]_{av}=F_{(1)_\delta}+F_{(2)_\delta}+F_{(3)_\delta}, \tag{31}$$

where

$$F_{(1)_\delta}\equiv\int\cdots\int\sum_{r=2}^{N_\alpha}F_{(\alpha r)_\delta}\vartheta^W\Pi_k'(d\omega)^{N_k}, \tag{32}$$

$$F_{(2)_\delta}\equiv\int\cdots\int\sum_{s=1}^{N_\beta}F_{(\beta s)_\delta}\vartheta^W\Pi_k'(d\omega)^{N_k}, \tag{33}$$

$$F_{(3)_\delta}\equiv\int\cdots\int\sum_{t=1}^{N_\gamma}F_{(\gamma t)_\delta}\vartheta^W\Pi_k'(d\omega)^{N_k}. \tag{34}$$

It remains to evaluate these integrals.

[37] M. Mason and W. Weaver, *The Electromagnetic Field* (University of Chicago Press, Chicago, 1929), p. 146.
[38] P. Walden, Ber. d. Phys. Ges. **38**, 345 (1905).
[39] H. G. Rule and A. McLean, J. Chem. Soc. 1400 (1932).
[40] R. H. Fowler, *Statistical Mechanics* (Cambridge University Press, 1929), Chap. VIII.
[41] J. G. Kirkwood, J. Chem. Phys. **3**, 300 (1935).

Case I

The assembly is an imperfect gas. We evaulate only $F_{(3)_\delta}$, the others follow *mutatis mutandi*. Since W is symmetrical in all the N_γ γ-molecules

$$F_{(3)_\delta}=N_\gamma\int\cdots\int F_{(\gamma)_\delta}\vartheta^W\Pi_k'(d\omega)^{N_k}/B'(\vartheta), \quad (35)$$

dropping the now superfluous subscript (t). $F_{(\gamma)_\delta}$ depends, to good approximation, only on the relative coordinates of the chosen α and γ-molecules: thus

$$F_{(3)_\delta}=\frac{N_\gamma\int F_{(\gamma)_\delta}d\omega_\gamma\int\vartheta^W\Pi_k''(d\omega)^{N_k}}{\int d\omega_\gamma\int\vartheta^W\Pi_k''(d\omega)^{N_k}}. \quad (36)$$

The inner integral[40, 41] is $Q\vartheta^{E_{\alpha\gamma}}$ where $E_{\alpha\gamma}$ is the interaction energy of the chosen α and γ-molecules. Now

$$\int d\omega_\gamma Q\vartheta^{E_{\alpha\gamma}}\sim Q8\pi^2V$$

where V is the volume of the system. Hence, finally

$$F_{(3)_\delta}=\frac{N_\gamma}{8\pi^2V}\int\vartheta^{E_{\alpha\gamma}}F_{(\gamma)_\delta}d\omega_\gamma. \quad (37)$$

Choosing as our arbitrary system of axes those of the α-molecule, $(N_\gamma/8\pi^2V)\vartheta^{E_{\alpha\gamma}}d\omega_\gamma$ represents the average number of γ-molecules at a given distance from, and with a particular orientation with respect to the chosen α-molecule in an element of extension $d\omega_\gamma$, and $F_{(\gamma)_\delta}$ the field of a single γ-molecule satisfying these conditions, at the origin of the system of coordinates. The integral, which is extended over all possible values of $(x_\gamma, y_\gamma, z_\gamma, \theta_\gamma, \varphi_\gamma, \psi_\gamma)$ is thus the sum of the fields of all the γ-molecules in their average distribution.

Case II

The assembly is a liquid. N_γ is in dilute solution. We consider the experiment of replacing β-molecules with γ-molecules, V and N_α held constant. The β-molecules are supposed nonpolar, the α and γ, polar. $F_{(1)_\delta}$ will *not* be invariant, but will be slowly varying with respect to $F_{(3)_\delta}$. $F_{(2)_\delta}$ is of course a function of N_β. We set

$$F_{(1)_\delta}+F_{(2)_\delta}=g_{(\gamma)_\delta}(N_\beta),$$

where $g_{(\gamma)_\delta}(N_\beta)$ is a smoothly varying function: the subscript γ signifies that the functions g will in general be different for differing molecules γ. Let $W=W_1+W_2$, where W_1 is not a function of the coordinates of any of the γ-molecules. (35) becomes

$$F_{(3)_\delta}=\frac{N_\gamma\int\vartheta^{W_1}\prod_{r=2}^{N_\alpha}d\omega_{\alpha r}\int\prod_{s=1}^{N_\beta}d\omega_{\beta s}\int\vartheta^{W_2}F_{(\gamma)_\delta}\prod_{t=1}^{N_\gamma}d\omega_{\gamma t}}{\int\vartheta^{W_1}\prod_{r=2}^{N_\alpha}d\omega_{\alpha r}\int\prod_{s=1}^{N_\beta}d\omega_{\beta s}\int\vartheta^{W_2}\prod_{t=1}^{N_\gamma}d\omega_{\gamma t}}.$$

As a first approximation we suppose $F_{(\gamma)_\delta}$ depends only on the relative coordinates of the chosen α-molecule and the γ-molecule. The first approximation to

$$\int\vartheta^{W_2}F_{(\gamma)_\delta}\prod_{t=1}^{N_\gamma}d\omega_{\gamma t}$$

is then $(8\pi^2V)^{N\gamma-1}\int\vartheta^{E_{\alpha\gamma}}F_{(\gamma)_\delta}d\omega_\gamma$,

and to $\int\vartheta^{W_2}\prod_{t=1}^{N_\gamma}d\omega_{\gamma t}$

is $(8\pi^2V)^{N\gamma}$, for small N_γ.[42]

Therefore, finally

$$[F_\delta]_{av}=g_{(\gamma)_\delta}(N_\beta)+N_\gamma\frac{\int\vartheta^{E_{\alpha\gamma}}F_{(\gamma)_\delta}d\omega_\gamma}{8\pi^2V}. \quad (38)$$

SECTION 6

The factors that enter into the evaluation of

$$(N_\gamma/8\pi^2V)\int F_{(\gamma)_\delta}\vartheta^{E_{\alpha\gamma}}d\omega_\gamma \quad (39)$$

are the fields and the geometrical shape[43] of the individual molecules. We evaluate the integral under the following assumptions:

[42] R. H. Fowler, reference 40, Chap. XIII.
[43] J. Weigle, Helv. Phys. Acta **6**, 68 (1933).

(i) Both molecules are uniformly polarizable spheres with dipoles at the center.

(ii) The effective radii of these spheres are such that $kT > 5E_{\alpha\gamma}$.

As far as the active substance (the α-molecule) is concerned, the shape is generally so complicated that the assumption above is the best we can make. Provided the dipoles of the molecules are close together and close to the active carbon atom, it is probably legitimate to add the dipoles and consider them as one single dipole. The electrostatic field of solvent molecules with many dipoles such as 3-nitro-4-amino benzene sulfonic acid cannot be represented as the field of the sum of the dipoles except at distances roughly 10 times the molecular diameter: assumption (i) does not, therefore, correspond to solvent molecules possessing more than a single dipole. The best correspondence will result if the molecules have forms *related* to a sphere with a dipole at the center—such as ellipsoids with a dipole at one focus. In this class the normal alkyl derivatives and the monosubstituted benzene series fall.

For solvent molecules of different shapes, a different assumption (i) must be made: correspondingly the integral will be a different function.[44]

Molecules with a benzenoid nucleus make an added contribution to the solvent field. This field must be practically the same for all aromatic compounds and remain constant in experiments under Case I in which one aromatic compound is replaced by another; therefore, this field does not manifest itself in such experiments and can be ignored. It does, however, cause a separation in the properties of compounds of the aliphatic and those of the aromatic series. In experiments under Case II, this field is added to $g_{(\gamma)\delta}(N_\beta)$. We shall show experimentally that the field is smoothly varying, so that no difficulty results from such a procedure.

Let A, B, and C be the polarizabilities of the α, β and γ-molecules, respectively; $\mathbf{F}_\alpha$, the field of the α-molecule at the γ-molecule; $\mathbf{F}_\gamma$, the field of the γ-molecule at the α-molecule; $F_{(3)_1}$, $F_{(3)_2}$, $F_{(3)_3}$, the components of the average field, $\mathbf{F}_{(3)}$, contributed by all the γ-molecules, in a set of rectangular Cartesian coordinates $(\mathbf{i}, \mathbf{j}, \mathbf{k})$ fixed in the α-molecule; $\boldsymbol{\mu}_\alpha = \mu_\alpha \mathbf{k}$, $\boldsymbol{\mu}_\beta$, $\boldsymbol{\mu}_\gamma$ the dipole moments of the α, β, and γ-molecules, respectively; $\mathbf{p}_\alpha$ and $\mathbf{p}_\gamma$ the induced dipoles of the α and and γ-molecules. If $\mathbf{r}$ is the position vector from O, the center of an α-molecule, to P, the center of a γ-molecule, then

$$\mathbf{F}_\alpha = -\frac{\boldsymbol{\mu}_\alpha + \mathbf{p}_\alpha}{r^3} + \frac{3\mathbf{r}\mathbf{r}\cdot(\boldsymbol{\mu}_\alpha + \mathbf{p}_\alpha)}{r^5},$$

$$\mathbf{F}_\gamma = -\frac{\boldsymbol{\mu}_\gamma + \mathbf{p}_\gamma}{r^3} + \frac{3\mathbf{r}\mathbf{r}\cdot(\boldsymbol{\mu}_\gamma + \mathbf{p}_\gamma)}{r^5}.$$

Further $\qquad \mathbf{p}_\alpha = A\mathbf{F}_\gamma, \quad \mathbf{p}_\gamma = C\mathbf{F}_\alpha.$

These four equations determine $\mathbf{p}_\alpha$ and $\mathbf{p}_\gamma$: under assumption (ii) the factors A/r^3 and C/r^3 are less than 0.02, so that, to about 2 percent

$$\mathbf{p}_\alpha = -\frac{A\boldsymbol{\mu}_\gamma}{r^3} + \frac{3A\mathbf{r}(\mathbf{r}\cdot\boldsymbol{\mu}_\gamma)}{r^5},$$

$$\mathbf{p}_\gamma = -\frac{C\boldsymbol{\mu}_\alpha}{r^3} + \frac{3C\mathbf{r}(\mathbf{r}\cdot\boldsymbol{\mu}_\alpha)}{r^5}$$

and $$\mathbf{F}_\gamma = -\frac{\boldsymbol{\mu}_\gamma}{r^3} + \frac{3\mathbf{r}(\mathbf{r}\cdot\boldsymbol{\mu}_\gamma)}{r^5} + \frac{C\boldsymbol{\mu}_\alpha}{r^6} + \frac{3C\mathbf{r}(\mathbf{r}\cdot\boldsymbol{\mu}_\alpha)}{r^8}.$$

The interaction energy is

$$-(\boldsymbol{\mu}_\alpha + \mathbf{p}_\alpha)\cdot\mathbf{F}_\gamma + Q_\alpha + Q_\gamma,$$

where $Q_\alpha + Q_\gamma$ is the sum of the internal energies of deformation of α and γ. This is[45] $\frac{1}{2}\mathbf{p}_\alpha\cdot\mathbf{F}_\gamma + \frac{1}{2}\mathbf{p}_\gamma\cdot\mathbf{F}_\alpha$. Hence to the same approximation as above,

$$E_{\alpha\gamma} = \frac{\boldsymbol{\mu}_\alpha\cdot\boldsymbol{\mu}_\gamma}{r^3} - \frac{3(\boldsymbol{\mu}_\alpha\cdot\mathbf{r})(\boldsymbol{\mu}_\gamma\cdot\mathbf{r})}{r^5},$$

which is just the interaction energy of the permanent dipoles. $\exp(-E_{\alpha\gamma}/kT)$ can be approximated by $1 - E_{\alpha\gamma}/kT$; the next significant contribution to $\mathbf{F}_{(3)}$ comes from the term in $(E_{\alpha\gamma}/kT)^3$, which is of the order of $(1/3!)(1/5)^2$ of the term retained.

Finally, let the position of P be given by spherical polar coordinates with origin O and pole $\mathbf{k}(r, \theta_1, \varphi_1)$; the orientation of γ, by the Eulerian coordinates $(\theta_2, \varphi_2, \psi_2)$ of a set of axes $(\mathbf{i}', \mathbf{j}', \mathbf{k}')$ fixed in γ, center P, $\mathbf{k}'$ along $\boldsymbol{\mu}_\gamma$. ψ_2 integrates out at once and we get ($d_{\alpha\gamma} = r_\alpha + r_\gamma$ = sum of radii of spheres)

[44] It is proposed to examine these in subsequent papers.

[45] P. Debye, *Polar Molecules* (Chemical Catalog Co., New York, 1929), pp. 30–32.

$$\mathbf{F}_{(3)}=\frac{N_\gamma}{4\pi V}\int_{d_{\alpha\gamma}}^{\infty} r^2dr\int_0^{\pi}\sin\theta_1 d\theta_1\int_0^{2\pi}d\varphi_1\int_0^{\pi}\sin\theta_2 d\theta_2\int_0^{2\pi}d\varphi_2\cdot\left[1-\frac{E_{\alpha\gamma}}{kT}\right]\cdot\mathbf{F}_\gamma$$

$$=\frac{N_\gamma}{4\pi V}\int_{d_{\alpha\gamma}}^{\infty} r^2dr\int d\Omega_1 d\Omega_2\left[1-\frac{1}{kT}\left(\frac{\boldsymbol{\mu}_\alpha\cdot\boldsymbol{\mu}_\gamma}{r^3}-\frac{3(\boldsymbol{\mu}_\alpha\cdot\mathbf{r})(\boldsymbol{\mu}_\gamma\cdot\mathbf{r})}{r^5}\right)\right]\left[-\frac{\boldsymbol{\mu}_\gamma}{r^3}+\frac{C\boldsymbol{\mu}_\alpha}{r^6}+\frac{3\mathbf{r}(\mathbf{r}\cdot\boldsymbol{\mu}_\gamma)}{r^5}+\frac{3C\mathbf{r}(\mathbf{r}\cdot\boldsymbol{\mu}_\alpha)}{r^8}\right]. \tag{40}$$

Introducing the coordinates $(r, \theta_1, \varphi_1, \theta_2, \varphi_2)$ and performing the indicated operations, we get

$$F_{(3)_1}=0;\quad F_{(3)_2}=0;\quad F_{(3)_3}=\frac{2}{{d_{\alpha\gamma}}^3}\cdot\mu_\alpha\cdot\frac{N_\gamma}{V}\cdot\frac{4\pi}{3}\left[C+\frac{{\mu_\gamma}^2}{3kT}\right]. \tag{41}$$

We may now complete the calculations of $(F_\delta)_{av}$ undertaken in Section 6. From Eqs. (31) and (41), (Case I, for imperfect gases), letting $n_\alpha=N_\alpha/V$, $n_\beta=N_\beta/V$, $n_\gamma=N_\gamma/V$.

$$[F_\delta]_{av}=(3\delta)\left\{\frac{2\mu_\alpha}{{d_{\alpha\alpha}}^3}\cdot\frac{4\pi}{3}\cdot n_\alpha\left[A+\frac{{\mu_\alpha}^2}{3kT}\right]+\frac{2\mu_\alpha}{{d_{\alpha\beta}}^3}\cdot\frac{4\pi}{3}\cdot n_\beta\left[B+\frac{{\mu_\beta}^2}{3kT}\right]+\frac{2\mu_\alpha}{{d_{\alpha\gamma}}^3}\cdot\frac{4\pi}{3}n_\gamma\left[C+\frac{{\mu_\gamma}^2}{3kT}\right]\right\}. \tag{42}$$

Supposing $d_{\alpha\alpha}$, $d_{\alpha\beta}$, $d_{\alpha\gamma}$ are all nearly equal, we obtain by using the Debye relationship and the law of mixtures,

$$[F_\delta]_{av}=(\delta 3)\cdot(2\mu_\alpha/d^3)\cdot((\epsilon-1)/(\epsilon+2)), \tag{43}$$

where ϵ is the dielectric constant of the gas.[46]

This equation is almost identical with (28), which was derived from an entirely different point of view. The relationships (43) hold only for molecules with a single (or zero) dipole moment: they do not hold for other types of molecules. These will show a different relation between $[F_\delta]_{av}$ and the dipole moments and polarizability of the solvent molecules and therefore, in general, no simple relation with ϵ.

From Eqs. (38) and (41), (Case II, for dilute solutions)

$$[F_\delta]_{av}=g_{(\gamma)_\delta}(N_\beta)+\frac{2\mu_\alpha}{{d_{\alpha\gamma}}^3}\cdot\frac{4\pi}{3}n_\gamma\left[C+\frac{{\mu_\gamma}^2}{3kT}\right](3\delta), \tag{44}$$

$$[F_\delta]_{av}=g_{(\gamma)_\delta}(N_\beta)+\frac{2\mu_\alpha}{{d_{\alpha\gamma}}^3}\cdot\frac{n_\gamma}{N}P_\gamma(3\delta)\quad N=6.06\times10^{23}$$

introducing $$P_\gamma=\frac{4\pi}{3}N\left[C+\frac{{\mu_\gamma}^2}{3kT}\right],$$

the molar polarization.[46]

In general, P_γ is a function of the concentration; its variation may be considered to be due to the association of the γ-molecules.[47] Provided the associated molecules satisfy the conditions as to the type of the γ-molecules (assumption *i*), P_γ will continue to be a measure of the field acting on a dipole and Eq. (44) will hold for concentrations where P_γ differs markedly from $(4\pi/3)N[C+(\mu_\gamma^2/3kT)]$. Experimentally, it is found that (44) remains valid throughout the entire concentration range (Section 7). Eq. (44) holds therefore for monodipolar solute molecules which exhibit association of the type $\overset{-+}{\underset{+-}{\rightleftarrows}}$ (zero moment) that is, for the most common type of association. It will not hold for molecules which associate chain-wise, or in fact for other types of association giving a zero moment unless the dipoles are so close that the cancelation of field is complete at small distances.

We have, taking only one substance to be optically active

$$\alpha=\frac{\pi}{\lambda_{vac.}}\cdot\frac{n^2+2}{3}\cdot\frac{n_\alpha}{6}\{\sigma'_{\xi\eta\zeta}(0)+\sigma'_{\xi\eta\zeta^\delta}[F_\delta]_{av}\}[\xi\eta\zeta], \tag{24'}$$

which may be put in the form

$$[\alpha]/(n^2+2)\equiv\Omega=\Omega_1+\Omega^\delta[F_\delta]_{av}. \tag{45}$$

Then, from (43) and (45)

$$\Omega=\Omega_1+\Omega^\delta\cdot(2\mu_\alpha/d^3)\cdot((\epsilon-1)/(\epsilon+2)) \tag{46}$$

and from (44) and (45)

$$\Omega=\Omega_1+\Omega^\delta g_{(\gamma)_\delta}(N_\beta)+\Omega^\delta\cdot\frac{2\mu_\alpha}{{d_{\alpha\gamma}}^3}\cdot\frac{n_\gamma}{N}\cdot P_\gamma. \tag{47}$$

[46] P. Debye, reference 45, Chap. II, III.

[47] C. P. Smyth, *Dielectric Constant and Molecular Structure* (Chemical Catalog Co., New York, 1929), Chap. IX.

Section 7

The experimental manifestations of the equations found in Section 6 divide themselves naturally into two parts: the gross effects observed on changing the solvent radically, that is, replacing one solvent by another, and the detailed effects which result from modifying the solvent by degrees by the introduction of increasing quantities of a third substance. For the first of these, Eq. (46), although derived for imperfect gases, will hold to a crude approximation for liquids, and will serve to illustrate the general trend. For the detailed effects, Eq. (47) must be used.

Part I. Gross effects

The fundamental equation here is

$$\Omega=\Omega_1+\Omega^3\cdot\frac{2\mu_\alpha}{d^3}\cdot\frac{\epsilon-1}{\epsilon+2}=\Omega_1+\Omega^3\cdot\frac{2\mu_\alpha}{d^3}\left\{B+\frac{\mu_\beta{}^2}{3kT}\right\}, \quad (48)$$

taking $N_\gamma=0$, and N_α/N_β small.

A. The dependence of the rotatory power on ϵ.—P. Walden,[38] reviewing the experimental data up to 1905, concluded that the sequence of solvents arranged in order of their effect on rotatory power, was practically identical with the sequence arranged in order of dielectric constant. In a more recent series of investigations, H. G. Rule,[48] has attempted to correlate the rotation of a compound in a series of related solvents with the dipole moment of the solvent molecules. From (43), we see that, if $\mu_\beta\neq0$ so that we can neglect B, there will be a rough relation between rotation[49] and dipole moment. For $\mu_\beta=0$, Rule's curve[48] becomes multiple valued, a circumstance which indicates that μ_β is not the sole factor in the variations of rotation. This factor is, according to Eq. (48), the polarizability of the solvent. Figs. 2, 3, and 4 give plots of the rotivity Ω against r, the dielectric ratio $(\epsilon-1)/(\epsilon+2)$. The points are distributed about a straight line, as predicted, and the multiple value is removed.

B. The dependence on dipole moment of solute.—Wolf and Volkmann,[20] in an attempted verification of the Born-Gans rule (Section 1), conclude that the relation

$$\text{Rotivity}=\Omega=\text{Constant}$$

holds sufficiently well for active compounds with small dipole moments, but not at all for substances like 1-menthone, whose moment is 2.83 debyes. From our point of view, this shows that if $\mu_\alpha=0$, the second term of (48) vanishes.

Our general set-up indicates that a molecule with no moment will create no external field: in particular, by Eq. (48), the plot of Ω against r must be a straight line of zero slope. This is strikingly confirmed for *d*-pinane.[50] (Fig. 5; contrast Fig. 3.)

We notice in passing that *d*-pinane is the best example yet found of the superiority of the rotivity over the rotation as a measure of optical rotatory power. There is a decided drift of rotation with refractive index of solvent, but none at all for the rotivity.

C. The separation of solvents into classes.—The experimental data indicates some very important differences in the behavior of solvents which can be interpreted in the light of our theory. First, it is found that aromatic and aliphatic solvents must be treated separately (Figs. 2 and 3). Within each of these classes of solvents the agreement with theory is good. Their different behavior will be discussed more fully later (Section 7, Part II, *D*). Secondly, we find that the points for the compounds CCl_4, $CHCl_3$, $CHBr_3$, and CS_2 all fall below the line for aliphatic solvents generally, indicating that the field of these compounds is greater than that given by $(2\mu_\alpha/d^3)((\epsilon-1)/(\epsilon+2))$. The fundamental physical reason behind this is that the field measured by the change in rotivity $\Delta\Omega$ and the polarization measured by the dielectric constant reflect, respectively, the effects of an electric dipole at short range and at long range. These effects do not necessarily coincide. This may be illustrated most easily in the case of CS_2. The CS_2 molecule is linear, with the two C→S dipoles oriented opposite to one another. If we consider one dipole localized at a point 1 and the other at a point 2, then the dipole field of the molecule at some point P is given by

[48] H. G. Rule, *Studies in Solvent Action. I*, J. Chem. Soc. 674 (1931); II, ibid. 2652 (1931); III, 1400 (1932); IV, 1409 (1932); V, 2332 (1932); VI, 376 (1933); VII, 1217 (1933).

[49] In discussing the data of other workers we will occasionally use the rotation instead of the rotivity.

[50] H. G. Rule and A. R. Chambers, Nature **133**, 910 (1934).

TABLE I. *1-Menthyl methyl naphthalate in aromatic solvents** ($c=4$).[48]

Solvent	$-[M]^{20}_{5461}$	$-M\Omega^{20}_{5461}$	r
Benzene	543	127	.302
Mesitylene	583	137	.311
Toluene	546	129	.315
Anisole	466	108	.528
Iodobenzene	465	100	.546
o-Chlorotoluene	502	116	.554
Brombenzene	466	104	.595
m-Chlorotoluene	497	115	.603
Chlorbenzene	463	107	.606
p-Chlorotoluene	433	101	.634
Aniline	443	98	.656
o-Dichlorbenzene	433	98	.746
Acetophenone	454	104	.845
Benzaldehyde	432	98	.846
Benzonitrile	372	85	.890
Nitrobenzene	423	96	.917

* The rotivity was calculated using the values for n for the pure solvent taken from the I.C.T.; the dielectric constants were taken from the same source or from A. Weissberger and E. Proskauer, *Organic Solvents* (Clarendon Press, Oxford, 1935), if listed there.

$$((\mathfrak{p}\cdot\mathfrak{r}_{1P})/r_{1P}^3)-((\mathfrak{p}\cdot\mathfrak{r}_{2P})/r_{2P}^3),$$

where $\mathfrak{p}$ is the moment of one C→S bond, r_{1P} and r_{2P} are the distances from points 1 and 2 to P, respectively. At great distances where $\mathfrak{r}_{1P}=\mathfrak{r}_{2P}$, the field vanishes. Such is the case for the interaction of this field with an external field like that existing between condenser plates. At short distances, however, where the effect of the dipoles on the rotivity is greatest, the field does *not* vanish and the molecule CS_2 acts strongly polar. This will be true of all molecules with more than one dipole.

To find the equation corresponding to (43) for these molecules, we merely have to make a different assumption (*i*), substitute in (39) and perform the indicated operations.[44]

So far we have neglected the effect of group size and "screening" by our tacit assumption $d=$constant. There is no necessity for doing this, and obviously an increase of size of the dipole carrier will be reflected by an increase in d and a corresponding decrease in field. This, as well as the comparative effects of *o*, *m*, and *p*-substituents, has been discussed experimentally by Rule;[48] his conclusions fit unchanged into the above theory.

D. The temperature effect.—As T increases, the term $\mu_\beta^2/3kT$ in (48) decreases, and the effect of the dipole moment of the solvent diminishes. Hence, for increasing temperatures the values of the rotations in polar solvents must converge towards the values in nonpolar solvents. Data supporting this conclusion are listed by Lowry.[51]

Part II. Detailed effects

From (47), denoting by the superscript ^{0} the values of the quantities concerned when $N_\gamma=0$, we obtain

$$\Omega-\Omega^0=\Omega^\delta[g_{(\gamma)_\delta}(N_\beta)-g_{(\gamma)_\delta}(N_\beta{}^0)]+\frac{2\mu_\alpha}{d_{\alpha\gamma}{}^3}\cdot\Omega^\delta\cdot\frac{n_\gamma}{N}\cdot P_\gamma.$$

Setting

$$G(\beta,\gamma)=(\Omega^\delta/n_\gamma)\{g_{(\gamma)_\delta}(N_\beta)-g_{(\gamma)_\delta}(N_\beta{}^0)\}N,$$

$$K_\gamma=(2\mu_\alpha/d_{\alpha\gamma}{}^3)\Omega^\delta \quad\text{and}\quad n_\gamma/N=w_\gamma/50M_\gamma,$$

where w_γ is the weight of substance γ in a solution made up to 50 cc. (see Section 8), and M_γ, the molecular weight of γ, we get

$$\Omega-\Omega^0=\frac{w_\gamma}{50M_\gamma}G(\beta,\gamma)+\frac{w_\gamma}{50M_\gamma}K_\gamma P_\gamma, \qquad (49)$$

$$S\equiv\frac{\Omega-\Omega^0}{w_\gamma}\cdot 50M_\gamma=G(\beta,\gamma)+K_\gamma P_\gamma. \qquad (50)$$

Since $g_{(\gamma)_\delta}(N_\beta)$ is smoothly varying (that is, dg/dw_γ varies slowly), $G(\beta,\gamma)$ is constant or nearly so. If P_γ changes decidedly, the variations

TABLE II. *1-Menthyl methyl naphthalate in aliphatic solvents* ($c=4$).[48]

Solvent	$-[M]^{20}_{5461}-$	$M\Omega^{20}_{5461}$	r
n-Pentane	651	169	.220
n-Hexane	653	167	.233
n-Heptane	653	166	.244
Cyclo-Hexane	688	170	.252
Ethyl ether	495	129	.537
Acetic acid	423	108	.631
Methyl Iodide	336	77	.670
Ethyl iodide	383	88	.681
Ethyl bromide	360	89	.823
Nitroethane	282	71	.862
Acetaldehyde	336	83	.873
Methyl cyanide	239	63	.924
Nitromethane	219	56	.924
Tetranitromethane	651	160	.274
Carbon tetrachloride	563	136	.289
Carbon disulfide	437	93	.358
Chloroform	362	88	.548
Bromoform	429	94	.554
Dichloromethane	267	66	.803

[51] T. M. Lowry, *Optical Rotatory Power*, pp. 354–356.

TABLE III. *1-Menthyl o-nitrobenzoate in aromatic solvents* ($c = 4$).*

Solvent	$-[M]^{20}_{5461}$	$-M\Omega^{20}_{5461}$	γ
Benzene	713.8	166.8	.302
Toluene	671.0	157.9	.315
Anisole	603.3	139.7	.528
Brombenzene	580.4	130.0	.595
Benzaldehyde	500.1	113.6	.846
Phenyl cyanide	465.1	106.4	.890
Nitrobenzene	422.7	95.3	.917

* A. McLean, J. Chem. Soc. 352 (1934).

in $G(\beta, \gamma)$ will be negligible: we may, therefore, take G to be a constant.

For experimental verification of Eqs. (49) and (50) none of the data in the literature is adequate. The experiments described immediately below were performed for this purpose.

A. S is a linear function of P_γ.—The first and most fundamental relationship which is subject to experimental verification is Eq. (50) which predicts that S is a linear function of P_γ.[52] Tables V, VI, VII and VII give the observed data, and Figs. 6, 7, 8 and 9 are plots of S against P_γ for a number of systems. The agreement is within the experimental error for all points; the equation holding even for solutions containing pure dipole solvent.

If Ω and P_γ both varied smoothly with the concentration of added polar compound, the observed linearity might be considered fortuitous. This is not the case. For the system diacetyl diethyl *d*-tartrate—benzene—nitrobenzene, Ω exhibits the surprising property of rising to a maximum at 5 grams of nitrobenzene (Fig. 10, middle curve) and then falling off rapidly with the further addition of nitrobenzene to a final value *below* the initial. At the same time, P_γ changes from about 360 cc at 0 grams of nitrobenzene to 94 cc at 0 grams of benzene, the slope of the polarization-concentration curve changing from a large negative value to almost zero (Fig. 10, inset). In spite of this, the graph of S against P_γ (Fig. 6) is a straight line. Similar considerations hold for diacetyl diethyl *d*-tartrate—benzene—chlorbenzene; diacetyl diethyl *d*-tartrate—benzene—benzonitrile; and *d*-limonene

[52] Note that Rule's M_2, aside from the factor $(n^2 + 2)^{-1}$, is related to S by factors depending on the concentrations alone. Hence, the observed "parallelism" between M_2 and P_γ is here predicted.

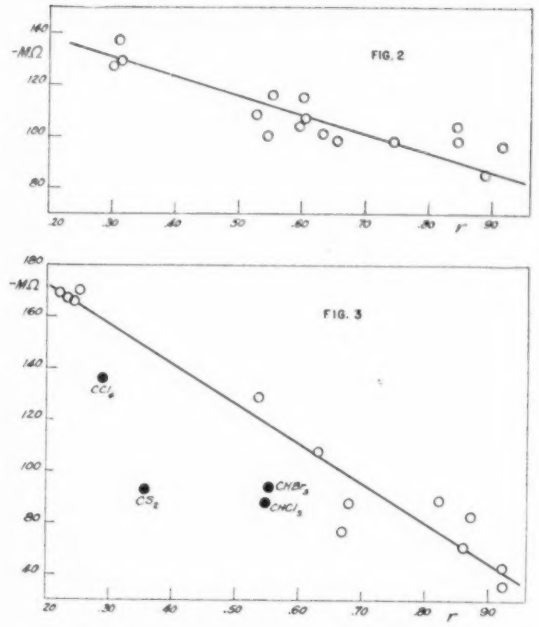


FIG. 2. 1-Methyl methyl naphthalate in aromatic solvents.
FIG. 3. 1-Methyl methyl naphthalate in aliphatic solvents.

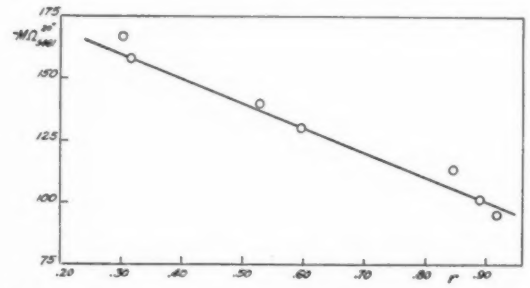


FIG. 4. 1-Menthyl *o*-nitrobenzoate in aromatic solvents.

—benzene—nibrobenzene (Figs. 11, 7, 8 and 9). The inference is inescapable that we are here dealing with a relationship of cause and effect.

It is evident from the derivation that $G(\beta, \gamma)$ and K_γ must be of opposite sign, since the former represents a decrease in the field while the latter represents an increase. Thus for a compound for which P_γ decreases markedly, we would expect to find S sometimes of one sign and sometimes of the other, depending on whether $|K_\gamma P_\gamma|$ or $|G(\beta, \gamma)|$ is the greater quantity. This is actually the case for diacetyl diethyl tartrate—benzene—nitrobenzene (Table V). Conversely, for solutions for which P_γ is fairly constant, we expect S to be relatively stationary: this is shown by diacetyl

diethyl tartrate—benzene—chlorbenzene (Table VI).

The excellent linearity of the relation between S and P_γ confirms the validity of Eq. (22), and also the deduction that $G(\beta, \gamma)$ is a constant; for without both of these being true, the observed strict linearity could not occur.

B. The variation of Ω with w_γ.—Returning to Eq. (49) and differentiating, we obtain

$$50M_\gamma(d\Omega/dw_\gamma)=G(\beta,\gamma)+K_\gamma P_\gamma+K_\gamma w_\gamma(dP_\gamma/dw_\gamma)$$
$$=S+K_\gamma w_\gamma(dP_\gamma/dw_\gamma).$$

We see the possibility of a change of sign of $d\Omega/dw_\gamma$ if dP_γ/dw_γ is large and negative. This change of sign is actually observed when nitrobenzene is used as the polar (γ) solute. (Table V; this also holds for 1-menthyl methyl naphthalate[48].)

Figs. 10 and 11 show how the various differently shaped curves for Ω against w_γ result from the curves for $w_\gamma P_\gamma$ and $w_\gamma G(\beta, \gamma)$ against w_γ, by means of Eq. (49)

$$\Omega-\Omega^0=\frac{w_\gamma G(\beta,\gamma)}{50M_\gamma}+\frac{K_\gamma w_\gamma P_\gamma}{50M_\gamma}. \qquad (49')$$

The values of $G(\beta, \gamma)$ and K_γ are taken from Figs. 6 and 7; the experimental values of $w_\gamma P_\gamma$, multiplied into $K_\gamma/50M_\gamma$ are plotted as ordinates, and $(w_\gamma/50M_\gamma)G(\beta, \gamma)$ is added to it: the curves for $\Omega-\Omega^0$ are deduced. The steep initial slope of the $P_\gamma-w_\gamma$ curve for nitrobenzene (Fig. 10) and its rapid falling off, result in a maximum for $\Omega-\Omega^0$; the corresponding $P_\gamma-w_\gamma$ curve for benzonitrile, because of the smaller value of

TABLE IV. *d-Pinane*[50] ($c=3.5$).

Solvent	$[\alpha]_D$	η_D	Ω_D	r
Methanol	19.3	1.3312	5.12	.910
Acetaldehyde	20.1	1.3316	5.30	.873
Acetonitrile	19.3	1.3460	5.05	.924
Acetone	20.9	1.3589	5.39	.872
Acetic acid	19.5	1.3715	5.00	.631
n-Hexane	20.1	1.3760	5.15	.233
Nitromethane	19.8	1.3813	5.05	.924
n-Heptane	21.1	1.3867	5.38	.244
Methylene chloride	21.0	1.4237	5.19	.803
Chloroform	21.8	1.4464	5.32	.548
Carbon tetrachloride	22.9	1.4607	5.52	.289
Methyl iodide	23.6	1.5293	5.44	.670
Carbon disulfide	28.1	1.6204	5.99	.358
Methylene iodide	26.6	1.7559	5.22	.600

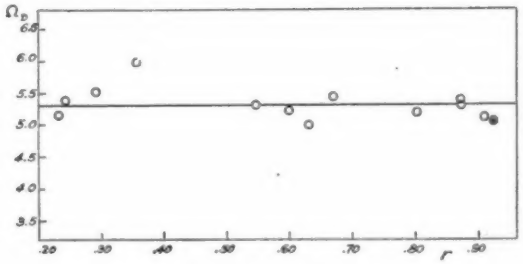


FIG. 5. *d*-Pinane.

$G(\beta, \gamma)$, gives only a flattening of the Ω-curve (Fig. 11).

In Tables IX and X, $\Omega-\Omega^0$ calculated from the right-hand side of (49) is compared with the measured value. The average deviations are, respectively, 0.013° and 0.018°, which is roughly the probable error of the experimental values. It will be noticed that it is possible to predict the rotivities from measurements of the dielectric constant more accurately than they can be read with the polariscope and refractometer.

The slope of the $\Omega-w_\gamma$ curve at the origin is given by

$$G(\beta,\gamma)+K_\gamma P_\gamma.$$

Depending on the relative magnitudes of the two terms, this slope may be positive or negative. Thus *d*-camphor shows a negative slope for benzene-chlorbenzene and a positive slope for benzene-nitrobenzene.

For *d*-limonene, the slopes for both chlorbenzene and nitrobenzene are positive, with the latter greater; for diacetyl diethyl *d*-tartrate, both slopes are again positive, but now the slope for chlorbenzene is greater (Tables V, VI, VIII, XII). All these apparently contradictory results take a natural position in the description here given.

C. The conditions on P_γ.—Højendahl[53] has shown that nitrobenzene associates to give a complex of zero moment. Therefore, the observed confirmation of Eq. (50), which holds only if the complexes have zero moment, is to be expected.

An analysis of the $P_\gamma-w_\gamma$ curve for ethanol in cyclohexane (compare Table XIII) leads to the conclusion that at low alcohol concentrations ethanol exhibits chain-wise association, and that at higher concentrations the chains break up so

[53] K. Højendahl, Thesis, Copenhagen, 1928.

TABLE V. *Diacetyl diethyl d-tartrate—benzene—nitrobenzene.**

w_α	w_β	w_γ	$-\text{Rotation}]^{25}_{5461}$ (2 dm)	n^{25}_{5461}	r	Ω^{25}_{5461}	S	P_γ	
4.994	39.893	00.000	2.890	1.49495	.3393	3.416	....	....	
5.007	39.81	00.000	2.865	1.49389	....	3.380	....	....	
5.007	39.78	00.000	2.897	1.49389	.3389	3.418	....	....	
5.003	39.827	00.000	2.884	1.49424	.3391	3.405	....	....	(mean)
5.003	38.91	1.197	2.840	1.49485	.3941	3.351	278	314.9	
4.999	38.096	2.469	2.827	1.49732	.4437	3.333	179	290.2	
5.001	38.03	2.472	2.800	1.49590	.4433	3.303	254	289.9	
5.005	37.22	3.587	2.755	1.49703	.4814	3.245	274	274.8	
4.999	36.450	4.744	2.782	1.49941	.5156	3.275	169	258.9	
5.008	36.30	4.824	2.775	1.49837	.5182	3.263	181	259.0	
5.000	35.48	5.975	2.785	1.49932	.5486	3.278	131	246.3	
5.013	35.520	5.996	2.782	1.50044	.5492	3.263	146	245.6	
4.995	34.599	7.349	2.802	1.50177	.5810	3.296	91	232.5	
4.999	32.951	9.573	2.847	1.50384	.6248	3.341	41.1	213.8	
4.997	31.170	12.008	2.892	1.50598	.6656	3.390	7.7	197.6	
5.007	29.451	14.383	2.984	1.50813	.6979	3.486	− 34.7	183.7	
5.005	27.684	16.788	3.074	1.51034	.7259	3.587	− 66.7	172.1	
5.019	26.805	17.998	3.118	1.51117	.7390	3.626	− 75.6	167.0	
5.005	22.415	24.004	3.410	1.51712	.7884	3.960	−142	145.6	
5.010	18.108	29.975	3.736	1.52225	.8254	4.319	−188	130.2	
5.007	00.000	54.77	5.210	1.54501	.9085	5.930	−284	94.46	

* The subscript α refers to the first substance mentioned in the title, β the next, and γ the next. Thus, here w_α is weight of diacetyl diethyl tartrate, w_β that of benzene, w_γ that of nitrobenzene.

TABLE VI. *Diacetyl diethyl d-tartrate—benzene—chlorbenzene.*

w_α	w_β	w_γ	$-\text{Rotation}]^{25}_{5461}$ (2 dm)	n^{25}_{5461}	r	$-\Omega^{25}_{5461}$	S	P_γ
5.003	39.827	00.00	2.884	1.49424	.3391	3.405	...	....
5.007	37.62	2.743	2.770	1.49504	.3620	3.266	285	77.72
5.003	35.430	5.520	2.667	1.49618	.3840	3.145	265	76.22
5.008	33.23	8.308	2.562	1.49798	.4045	3.014	265	74.68
5.005	31.074	11.030	2.472	1.49912	.4234	2.907	254	73.38
5.006	28.89	13.802	2.335	1.50035	.4410	2.744	269	71.89
5.006	26.686	16.551	2.292	1.50158	.4550	2.689	243	69.81
5.009	22.352	22.072	2.135	1.50421	.4892	2.500	231	68.61
5.007	18.010	27.539	2.010	1.50683	.5168	2.350	216	66.67
5.007	13.669	33.042	1.900	1.50933	.5432	2.218	202	65.10
5.006	00.000	50.31	1.660	1.51748	.6090	1.927	165	60.53

TABLE VII. *Diacetyl diethyl tartrate—benzene—benzonitrile.*

w_α	w_β	w_γ	$-\text{Rotation}]^{25}_{5461}$	n^{25}_{5461}	r	$-\Omega^{25}_{5461}$	S	P_γ
5.007	39.822	00.000	2.897	1.49389	.3418	3.418	...	....
5.006	35.464	5.023	2.550	1.49723	.5468	3.002	427	243.5
5.006	34.590	6.019	2.468	1.49780	.5471	2.905	419*	231.6
5.005	32.838	8.046	2.411	1.49913	.6210	2.835	359*	211.1
5.006	31.097	10.047	2.375	1.50035	.6583	2.790	322	194.2
5.005	28.927	12.549	2.311	1.50196	.6962	2.712	280*	177.2
5.007	26.750	15.062	2.275	1.50346	.7270	2.666	257	163.2
5.006	22.363	20.092	2.230	1.50655	.7721	2.608	208	141.6
5.006	13.648	30.107	2.151	1.51264	.8302	2.505	156	114.6
5.005	00.000	45.760	2.032	1.52243	.8795	2.351	120	91.43

* For these points $\Omega^0 = 3.395$.

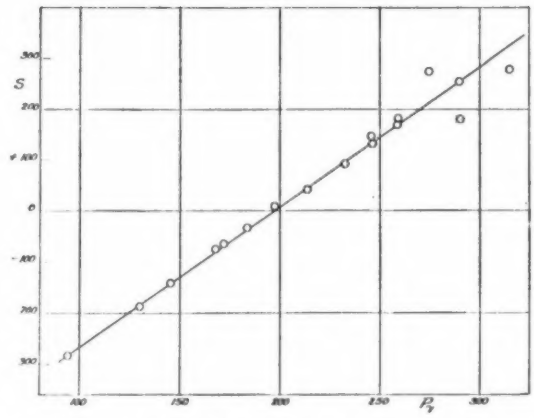


FIG. 6. Diacetyl diethyl *d*-tartrate in benzene-nitrobenzene mixtures.

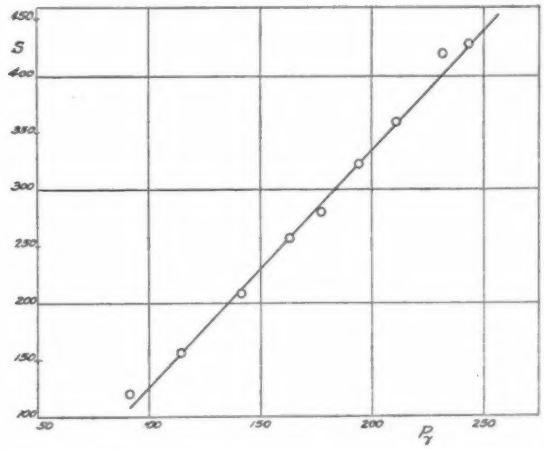


FIG. 7. Diacetyl diethyl *d*-tartrate in benzene-benzonitrile mixtures.

that the dielectric properties of alcohol approach once more those of a normal liquid.[47]

Accordingly, we expect that S will *not* be linear in P_γ. The $S-P_\gamma$ curve for *d*-camphor—cyclohexane—ethanol (Fig. 12) demonstrates that alcohol does not associate in the normal fashion. We distinguish three distinct sections of the curve. The first, (AB), corresponding to the initial decrease in P_γ; the second, (BC), corresponding to the rise of P_γ; and the third, (CD), corresponding to the breaking down of the alcohol chains and the return to normal behavior of the solution. In this last portion of the $S-P_\gamma$ curve, we see, indeed, that the rate of change of slope is vanishing and we are returning once more to the linear law $S=G(\beta, \gamma)+K_\gamma P_\gamma$.

The data just given represent independent evidence concerning the nature of alcohol complexes in solution: it confirms the conclusions of Smyth.[47]

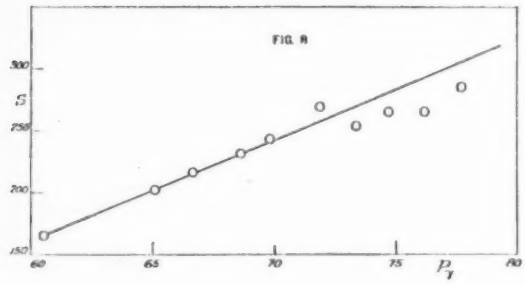
D. The influence of the benzenoid nucleus. For aromatic compounds assumption (*i*) Section 6, is obviously inadequate. The present state of our knowledge concerning the short-range field of a benzenoid ring, although indicating a very large one,[54] is nevertheless not enough to present us with a satisfactory substitute for (*i*). But for our present purpose, which is to correlate changes in rotivity with that part of the solvent field caused by dipoles, such detailed information is not necessary. To be able to eliminate the effect of benzene rings, it is sufficient to establish that

TABLE VIII. *d-Limonene—benzene—nitrobenzene.*

w_α	w_β	w_γ	Rotation $]^{25}_{5461}$	n^{25}_{5461}	r	Ω^{25}_{5461}	S	P_γ
4.178	39.229	00.000	23.935	1.49780	.3013	33.751	...	....
4.1844	39.228	00.000	23.970*	1.49768	....	33.751	...	....
4.179	37.059	3.051	24.008	1.50054	.4352	33.781	61	299.9
4.179	34.912	5.981	24.125	1.50328	.5268	33.880	133	262.3
4.1826	32.717	9.0305	24.268*	1.50627	....	33.979	155	....
4.179	32.710	9.040	24.260	1.50627	.5987	33.998	168	232.6
4.181	30.552	11.993	24.380	1.50914	.6526	34.080	166	210.6
4.1850	26.308	17.881	24.609*	1.51466	....	34.234	166	....
4.179	26.260	17.963	24.563	1.51475	.7301	34.217	160	177.2
4.178	21.891	23.973	24.795	1.52037	.7839	34.412	170	154.2
4.171	17.557	29.923	24.985	1.52570	.8223	34.603	175	137.5
4.1852	13.227	35.865	25.294*	1.53139	....	34.772	175	....
4.179	13.205	35.903	25.250	1.53148	.8516	34.761	173	124.7
4.179	6.619	44.900	25.645	1.54006	.8839	35.092	184	110.3
4.178	0.000	54.031	26.025	1.54833	.9075	35.414	189	99.49

* These rotations have been corrected for racemization.

[54] G. Briegleb, Zeits. f. physik. Chemie **B31**, 58 (1935).



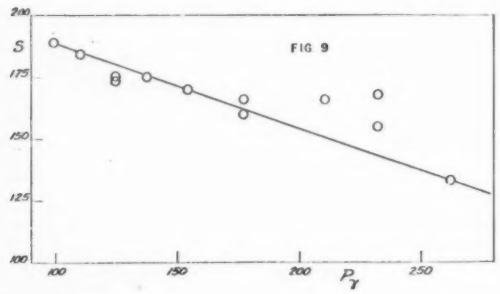


FIG. 8. Diethyl diacetyl *d*-tartrate in benzene-chlorbenzene mixtures.
FIG. 9. *d*-Limonene in benzene-nitrobenzene mixtures.

the field of the benzene-nuclei varies smoothly with concentration.

This result, indeed, has already been shown indirectly, since $G(\beta, \gamma)$ could not be constant if this proposition were not true. The experiments of gradually replacing cyclohexane as solvent by benzene or diphenyl (Tables XIV and XV; Fig. 13) demonstrate it directly.

We note that the effect of the phenyl groups of benzene and of diphenyl is almost the same in spite of the difference in geometrical structure of the molecules (Fig. 13). Finally we remark that in the experiments actually performed, replacing benzene by benzene derivatives as solvent (Part II, *A*), the change in the number of benzene groups corresponds to only the last seventh of the range of this last experiment. Over this region we can even say that the field of the benzene-nuclei varies *linearly* with the concentration.

E. Conclusions concerning the active molecule.— Unusual interest attaches to studies of tartaric acid and derivatives, partly on historical grounds, partly because of their remarkable properties.[55]

[55] T. M. Lowry, reference 51, Chap. 23.

Diacetyl diethyl *d*-tartrate is typical of these compounds. Table XVI gives the specific rotation of this compound in different solvents.

From our viewpoint, it seems likely that the "anomalous" behavior of optically active compounds has been considerably overestimated: it was therefore of particular importance to show that this chemically very stable compound acts normally. Tables V, VI and VII (Figs. 6, 7 and 8) show that there is not the slightest irregularity in the reactions of diacetyl diethyl tartrate to its solvents. We have already shown (Section 7, Part II, *B*) that change of sign of rotation may occur through simple deformation. A comparison of Tables V and VIII makes clear that there is a difference neither in kind nor in degree between the reactions of *d*-limonene and diacetyl diethyl *d*-tartrate.

The properties of the active molecule enter by way of the quantity $K_\gamma = (2\mu_\alpha/d_{\alpha\gamma}{}^3)\Omega^3$. If K_γ is to have any physical significance, it is an elementary requirement that it should be not far different for two compounds as much alike as nitrobenzene and benzonitrile. We find (Tables IX and X) the values are, respectively, 2.705 and 2.098

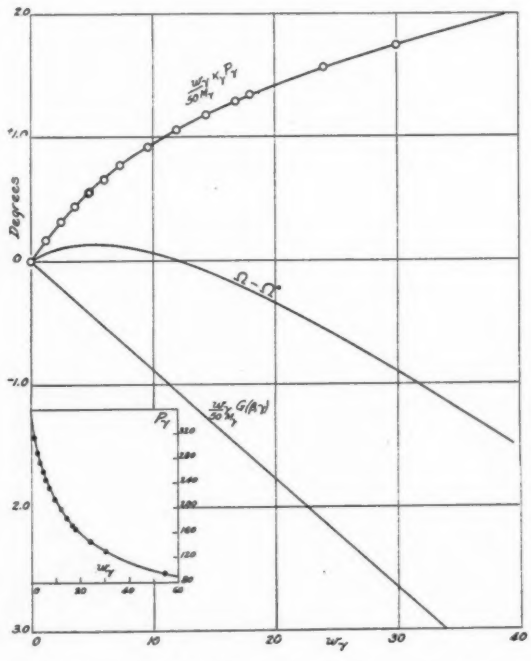


FIG. 10. Diacetyl diethyl *d*-tartrate in benzene-nitrobenzene mixtures.

(with diacetyl diethyl tartrate), corresponding to

$$\frac{d_{a\gamma}(\text{benzonitrile})}{d_{a\gamma}(\text{nitrobenzene})} = 1.088.$$

The value of K_γ for limonene with nitrobenzene, (0.336), (Table VIII), is much smaller than that for diacetyl diethyl tartrate with nitrobenzene (2.705). If we attribute this difference to the different values of μ_a, we obtain the result that *d*-limonene has a dipole moment of about 0.3 debye (taking the μ of diacetyl diethyl tartrate as 3 debyes). This agrees with the value of 0–0.5 debyes found by Wolf and Volkmann.[20] In any case, we must conclude from the very existence of the K_γ that *d*-limonene has a moment.

F. Concentration effect.—It is plain that a change of the concentration of active stuff is equivalent to a change in N_γ, and the concentration effect is therefore a special case of the general solvent effect.

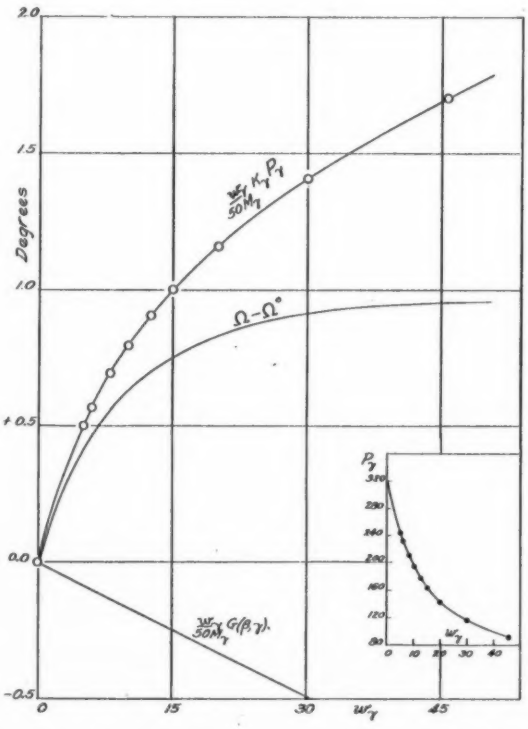


FIG. 11. Diacetyl diethyl *d*-tartrate in benzene-benzonitrile mixtures.

SECTION 8

I. Design of experiments. Calculations

The large amount of data on optical rotatory power in various solvents cannot be used for our purpose because of the lack of the two other relevant pieces of information: index of refraction n, and dielectric constant ϵ. That the refractive index of the solution whose rotation is measured, is a significant quantity, has been known since 1915;[14] nevertheless, Wolf and Volkmann[20] are the only two investigators who have used it systemically. That ϵ is significant, we believe to be shown in this paper, if not by the previous qualitative work of Rule.[48] The experiments described below contain the first simultaneous measurements of dielectric constant, refractive index and rotation.

The choice of solvents is an extremely important factor: an arbitrary and random selection has too often resulted in a hopeless confusion. For our purpose it was essential to choose closely related compounds, whole sole differences were in the magnitude of dipole moment. These conditions were satisfied by the monosubstituted aromatic compounds. It was further necessary to choose compounds with large and variable P_γ. The experimental conditions of stability, nonconductivity, high boiling point, and purity, reduced the number of available compounds to four: benzene, chlorbenzene, benzonitrile and nitrobenzene. These were the solvents used to check Eqs. (49) and (50). In the aliphatic series no such series was available; ethyl alcohol and cyclohexane were used, but for a different purpose.[56] Other solvents were tried and abandoned; thus, ethyl bromide (B.P. 38°C) was so volatile that evaporation produced serious errors; decahydronaphthalene behaved too much like cyclohexane to be of interest; ethyl acetate, otherwise eminently suitable, was doubtful geometrically; and so forth.

Suitable active substances were easier to find, the only requirements being purity and absence of tautomerism. Diacetyl diethyl tartrate was chosen, not only because of the reasons outlined in Section 7 (Part II, *E*), but also because its known susceptibility to solvent influences made us anticipate fairly large changes of rotation and correspondingly good precision. *d*-Camphor and *d*-limonene were selected because of their availability in quantity and purity. 1-Menthol was tried for a series of experiments, but its relative insensibility towards external influences made it impossible to draw conclusions from its behavior.

II. Experimental procedure

Fixed amounts (±10 milligrams) of active substance were weighed into a set of 50 cc graduated flasks. Varying quantities of a polar solvent were added to the flasks, which were then weighed, and filled up to the 50 cc mark with nonpolar solvent in a thermostat at 25.00°. The resulting solutions were again weighed; the weights of the three substances in a fixed volume were then known. The flasks were calibrated and the weights corrected to vacuum.

[56] Aliphatic series measurements on diacetyl diethyl tartrate could not be made because of its small solubility (about 1 percent) in cyclohexane, *n*-heptane and decahydronaphthalene.

To minimize evaporation losses, readings were made of

$$n_{5461}^{25.00°},\ \epsilon_{\infty}^{25.00°} \text{ and rotation}]_{5461}^{25.00°}$$

as soon as possible after the solutions were made up.

P_γ was computed from the equation

$$N(\epsilon-1/(\epsilon+2)=n_\alpha P_\alpha+n_\beta P_\beta+n_\gamma P_\gamma.$$

P_β was found by measurements on the pure solvent β, P_α by measurements on the two-component (α, β) mixture. Assuming that P_α and P_β were constants independent of n_γ, the values of P_γ could then be found from measurements on the 3-component mixtures.

S is very sensitive to small changes in Ω^0, the value of the rotivity of the active material dissolved in pure solvent β, particularly in those cases where $\Omega-\Omega^0$ is not large. Ω^0 was therefore measured more than once, and the mean used. (Table V.)

TABLE IX. *Diacetyl diethyl d-tartrate—benzene—nitrobenzene.*

$G(\beta,\gamma)=-543.4$		$K_\gamma=2.750$		$50M_\gamma=6152.5$
w_γ	$\frac{-G(\beta,\gamma)}{50M_\gamma}w_\gamma$	$\frac{K_\gamma}{50M_\gamma}w_\gamma P_\gamma$	$\frac{w_\gamma}{50M_\gamma}\times[G(\beta,\gamma)+K_\gamma P_\gamma]$	observed
1.197	0.1057	0.1685	.0628	.054
2.469	0.2181	0.3203	.1022	.072
2.472	0.2184	0.3204	.1020	.102
3.587	0.3169	0.4406	.1237	.160
4.744	0.4191	0.5489	.1298	.130
4.824	0.4262	0.5586	.1324	.142
5.975	0.5278	0.6578	.1300	.127
5.996	0.5297	0.6583	.1286	.142
7.349	0.6492	0.7637	.1145	.109
9.573	0.8457	0.9149	.0692	.064
12.008	1.0608	1.0605	−.0003	.015
14.383	1.2706	1.1812	−.0894	−.081
16.788	1.4831	1.2915	−.1916	−.182
17.998	1.5899	1.3435	−.2464	−.221
24.004	2.1205	1.5621	−.5584	−.555
29.975	2.6480	1.7446	−.9034	−.914
54.77	4.8384	2.3126	−2.5258	−2.525

TABLE X. *Diacetyl diethyl d-tartrate—benzene—benzonitrile.*

$G(\beta,\gamma)=-84.11$		$K_\gamma=2.098$		$50M_\beta=5152.5$
w_γ	$\frac{-G(\beta,\gamma)}{50M}w_\gamma$	$\frac{K_\gamma}{50M_\gamma}w_\gamma P_\gamma$	$\frac{w_\gamma}{50_\gamma M}\times[G(\beta,\gamma)+K_\gamma P_\gamma]$	observed
5.023	0.0820	0.4980	.4160	.416
6.019	0.0983	0.5677	.4694	.490
8.046	0.1313	0.6914	.5601	.560
10.047	0.1640	0.7944	.6304	.628
12.549	0.2048	0.9051	.7003	.683
15.062	0.2459	1.0008	.7549	.752
20.092	0.3280	1.1583	.8303	.810
30.107	0.4915	1.4047	.9132	.913
45.760	0.7470	1.7034	.9564	1.067

III. Preparation of materials

Diacetyl diethyl d-tartrate.—Diethyl *d*-tartrate was made from *d*-tartaric acid and absolute ethyl alcohol according to the method of Lowry and Cutter.[57] The crude product was distilled at 2 mm, retaining only the colorless middle fraction, $\alpha^{25}{}_{5461}=9.87°$ (2 dm). This was refluxed with acetic anhydride, following the procedure of McCrae and Patterson,[58] giving diacetyl diethyl *d*-tartrate. The crude product was purified[59] by recrystallizing 5 times from aqueous alcohol.[60] M.P. 67.3–67.6°C (corr.). $[\alpha]^{25}{}_{5461}$ ($c=10.01$ in benzene) $=-14.41°$. Analysis: Calculated, C = 49.61

TABLE XI. *d-Camphor—benzene—nitrobenzene.*

w_α	w_β	w_γ	Rotation	n	r	Ω	P_γ
5.006	39.02	00.000	10.903	1.49675	.4053	12.841	—
5.008	35.02	4.789	10.988	1.50130	.5565	12.892	224.4
5.005	30.37	11.98	11.075	1.50813	.6872	12.942	175.1
5.008	25.95	17.99	11.198	1.51374	.7529	13.028	149.4
5.004	8.483	42.038	11.420	1.53628	.8802	13.082	100.0
5.006	0.000	53.65	11.470	1.54704	.9099	13.039	88.38

d-Camphor—benzene—chlorbenzene.

w_α	w_β	w_γ	Rotation	n	r	Ω	P_γ
5.006	39.02	00.000	10.903	1.49675	.4053	12.841	—
5.004	00.00	49.33	10.880	1.52019	.6359	12.609	56.65

TABLE XII. *d-Limonene—benzene—chlorbenzene.*

w_α	w_β	w_γ	Rotation	n	r	Ω	P_γ
4.200	39.115	0.000	28.880	1.49627	.3004	33.534	—
4.205	34.761	5.507	23.978	1.49903	.3482	33.566	79.09
4.202	30.430	11.034	24.015	1.50177	.3901	33.576	75.90
4.201	26.031	16.558	24.073	1.50450	.4270	33.601	73.31
4.197	21.690	22.073	24.115	1.50720	.4592	33.627	70.75
4.197	17.380	27.550	24.160	1.50978	.4880	33.629	68.56
4.196	00.000	50.537	24.343	1.52055	.5876	33.625	61.65

TABLE XIII. *d-Camphor—cyclohexane—ethanol.*

w_α	w_β	w_γ	Rotation	n	r	Ω	$-S/10$	P_γ
5.006	34.67	0.000	15.107	1.42981	.3654	18.654	—	—
5.005	33.80	0.832	14.590	1.42821	.3893	18.040	169.9	81.92
5.006	33.04	1.563	14.315	1.42672	.4099	17.715	138.3	81.32
5.008	32.24	2.374	14.095	1.42542	.4330	17.427	119.0	80.99
5.008	31.42	1.175	13.918	1.42353	.4575	17.225	101.5	82.24
5.007	30.68	3.938	13.775	1.42203	.4812	17.100	90.86	83.03
5.006	29.90	4.740	13.628	1.42074	.5060	16.936	83.45	83.50
5.009	28.26	6.304	13.433	1.41755	.5543	16.722	70.57	84.33
5.007	26.73	7.897	13.222	1.41498	.5986	16.495	62.95	83.18
5.005	24.776	9.886	13.045	1.41163	.6487	16.320	54.36	81.12
5.008	22.83	11.835	12.825	1.40809	.6888	16.075	50.17	78.01
5.004	20.889	13.813	12.642	1.40535	.7256	15.889	46.09	75.04
5.005	18.96	15.79	12.475	1.40144	.7512	15.720	42.78	71.31
5.007	16.933	17.842	12.337	1.39812	.7762	15.756	39.72	68.05
5.006	15.30	19.73	12.160	1.39572	.7952	15.382	38.18	65.00
5.005	11.185	23.717	11.977	1.39073	.8261	15.207	33.46	59.70
5.005	7.375	27.664	11.735	1.38294	.8489	14.982	30.56	55.16
5.005	3.555	31.621	11.442	1.37737	.8684	14.665	29.05	51.50
5.005	0.000	35.326	11.202	1.37241	.8798	14.408	27.67	48.36

[57] T. M. Lowry and J. O. Cutter, J. Chem. Soc. **121**, 532 (1922).

[58] J. McCrae and T. S. Patterson, J. Chem. Soc. **77**, 1098 (1900).

[59] O. Scheuer, Zeits. f. physik. Chemie **72**, 516 (1910).

[60] Dipropionyl diethyl *d*-tartrate, a liquid, made in an analogous fashion, could not be purified.

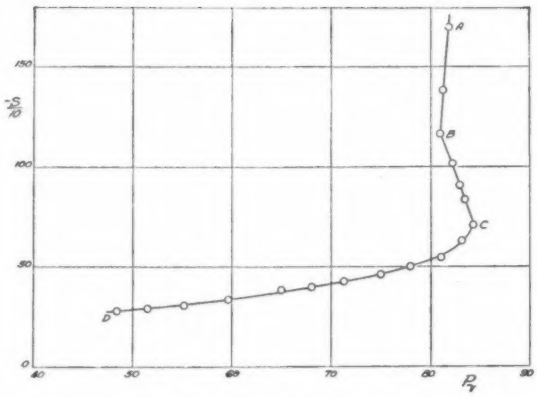


FIG. 12. *d*-Camphor in cyclohexane-ethanol mixtures.

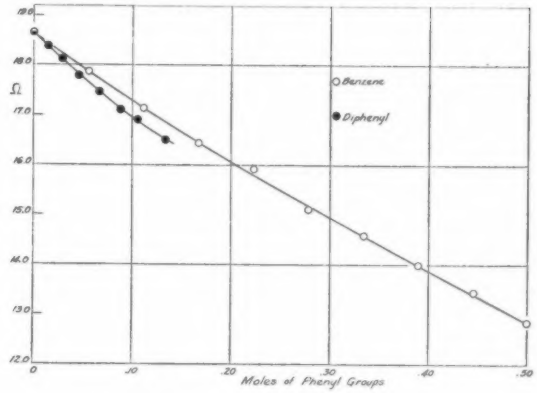


FIG. 13. *d*-Camphor in cyclohexane-benzene and cyclohexane-diphenyl mixtures.

percent, H = 6.25 percent; found, C = 49.78 percent (mean of 4), H = 6.94 percent (mean of 3).

d-Camphor.—Eastman block camphor was recrystallized from aqueous alcohol, carefully removing last traces of moisture by extended drying in air and finally by heating at 110° for 30 minutes. $[\alpha]^{25}_{5461}$ (c = 10.012 in benzene) = 74.64°.

d-Limonene.—Eastman *d*-limonene was fractionally distilled at 25 mm pressure, keeping only the middle fraction, B.P. 79–80°C. $[\alpha]^{25}_{5461}$ (c = 8.356 in benzene) = 143.2°.

Cyclohexane.—Eastman cyclohexane was dried over sulfuric acid and fractionated,[61] retaining the middle fraction B.P. 80.0–80.6°, $\epsilon_\infty^{25} = 2.021$.

Ethanol.—Commercial absolute alcohol (U.S.P.), unsuitable for dielectric measurements because of conductivity, was refluxed for 4 hours with CaO and KOH, distilled, and fractionated, retaining only the middle fraction, B.P. 78.0–78.1°, $n^{25}_{5461} = 1.36122$.

Benzene.—Thiophene-free benzene was dried with anhydrous $CaSO_4$ for 2 days, and fractionated, retaining the middle fraction, B.P. 79.6–80.0°.

Chlorbenzene.—Eastman chlorbenzene was dried with anhydrous $CaSO_4$ for 2 days, fractionated, keeping the fraction B.P. 131.0–131.4°. $\epsilon_\infty^{25} = 5.596$–$5.606$, ($\epsilon_\infty^{25} = 2.2725$ for benzene as standard).

Nitrobenzene.—Nitrobenzene from benzene crystals was washed for 10 hours with normal K_2CO_3 solutions, then with water, dried 2 days with anhydrous $CaSO_4$, and distilled at 3 mm pressure in the all-glass fractionating apparatus. The middle fraction, a pale yellow-green, was retained.

Benzonitrile.—Schuchardt benzonitrile was fractionated, discarding a generous first fraction (to eliminate water). B.P. 189.2–190.4°.

Diphenyl.—Commercial diphenyl was recrystallized from benzene, M.P. sharp at 70.5°.

Diacetyl diethyl tartrate was recovered from solutions containing benzene, chlorbenzene and nitrobenzene by evaporating the solutions to dryness in a current of air at room temperature, washing in practical "heptane" until the odor of nitrobenzene had disappeared, and recrystallizing from aqueous alcohol. It had the same constants as the original sample, and was re-used. Cyclohexane was recovered

TABLE XIV. *d-Camphor—cyclohexane—benzene.*

w_α	w_β	w_γ	Rotation	n	Ω	moles benzene
5.006	34.67	0.000	15.107	1.42981	18.654	.00000
5.001	30.751	4.334	14.524*	1.43661	17.866	.05553
5.007	26.77	8.702	14.010	1.44273	17.139	.1115
5.001	22.931	13.055	13.492*	1.45025	16.437	.16727
5.007	19.01	17.42	13.095	1.45693	15.860	.2233
5.000	15.231	21.746	12.562*	1.46529	15.146	.27863
5.006	26.13	26.13	12.172	1.47233	14.585	.3348
4.998	7.571	30.446	11.731*	1.48134	13.991	.39010
4.999	3.761	34.802	11.335*	1.48957	13.437	.44591
5.006	0.000	39.02	10.903	1.49675	12.841	.4999
5.001	0.000	39.094	10.894*	1.49808	12.831	.50090

* The rotations have been corrected for racemization.

TABLE XV. *d-Camphor—cyclohexane—diphenyl.*

w_α	w_β	w_γ	Rotation	n	Ω	2 × moles diphenyl
5.006	34.67	0.000	15.107	1.42981	18.654	.00000
5.001	33.808	1.133	14.914*	1.43430	18.376	.01471
5.002	32.981	2.226	14.746*	1.43832	18.114	.02889
5.005	32.253	3.562	14.533	1.44296	17.783	.04624
5.001	30.794	5.118	14.319*	1.44884	17.462	.06643
5.005	29.588	6.791	14.105	1.45504	17.112	.08815
5.004	28.506	8.101	13.983*	1.45992	16.909	.10515
5.009	26.81	10.32	13.735	1.46797	16.499	.13396

* The rotations have been corrected for racemization.

[61] All fractionations were performed using an all-glass distilling apparatus with a 10-inch Vigreux column.

TABLE XVI. *Diacetyl diethyl tartrate in various solvents* (c = *5 to 6*).*

Solvent	$[\alpha]_D$
(pure liquid)	5.0
Alcohol (95%)	1.3
Alcohol (Abs.)	0.3
Acetone	0.1
Carbon tetrachloride	−7.8
Chloroform	−10.3
Benzene	−10.9

* P. Freundler, Ann. chim. phys. (7) **4**, 244 (1895).

from solutions containing ethyl alcohol and camphor by washing with water, extracting the camphor completely with repeated portions of concentrated sulfuric acid, and fractionating. The product had no rotatory power and the same constants as the original sample, and was re-used.

IV. Apparatus and precision

Rotation was measured with a triple-field half-shadow Schmidt and Haensch polariscope, reading to 0.01°. Refractive index was measured with a Pulfrich refractometer. The light source common to both instruments was a mercury vapor lamp. For the polariscope the light was filtered through two Corning Glass Filters, No. 351 (3.5 mm) Didymium No. 512 (7.23 mm), and a nickel chloride solution to isolate the 5461 Hg line. The temperature of the solutions measured was kept at 25.00±0.02° by a rapid current of water.

Dielectric constant was measured by the heterodyne beat method,[62] using a 1000 $\mu\mu$f calibrated precision condenser reading to 0.1 $\mu\mu$f. A standard cell was used to eliminate apparent variations in capacity caused by accidental changes in the frequency of the oscillations: changes in frequency were shown by the reading for the standard cell and corrections were made according to a previously determined calibration curve. The standard cell was a large air condenser made of concentric platinum cylinders, having a capacity of about 122 $\mu\mu$f: the measuring cells were smaller, having capacities (with air as a dielectric) of 74 and 33 $\mu\mu$f, and holding a volume of liquid of about 25–30 cc. The cells were immersed in an oil-bath kept at 25.00±0.01°C.

The refractive indices may vary by 5 in the fifth decimal place. Four readings were taken of each rotation, and the average deviation was 0.005°. $r=(\epsilon-1)/(\epsilon+2)$, computed from eight readings, can be measured to about 0.07 percent to 0.04 percent, the precision increasing with increasing ϵ.

[62] C. P. Smyth, reference 47, p. 55.

Summary

1. The theoretical method used by C. G. Darwin in his paper "The Optical Constants of Matter" is extended to the field of molecular optics. Explicit account is taken of the effect of intermolecular forces on these constants (Section 2).

2. On the basis of the concept of deformation, a relation is found between the rotivity and the average molecular field on a molecule (Section 3).

3. The expression for the average field is derived for the limiting case of a continuous medium (Section 4).

4. A more general derivation of the average field, based on statistical mechanics, is given for a simple molecular model. This field is found to be, for gases

$$(2\mu_\alpha/d^3)\cdot((\epsilon-1)/(\epsilon+2)).$$

For liquids an analogous expression is found, in terms of the molar polarizations (Sections 5 and 6).

5. Combining our results, we find a relation between the rotivity and the dielectric constant, for gases, and between rotivity and molar polarization, for liquids (Section 6).

6. These results were verified by experiments (Section 7).

7. The validity of the use of the change of rotivity as a measure of the molecular field is established.

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